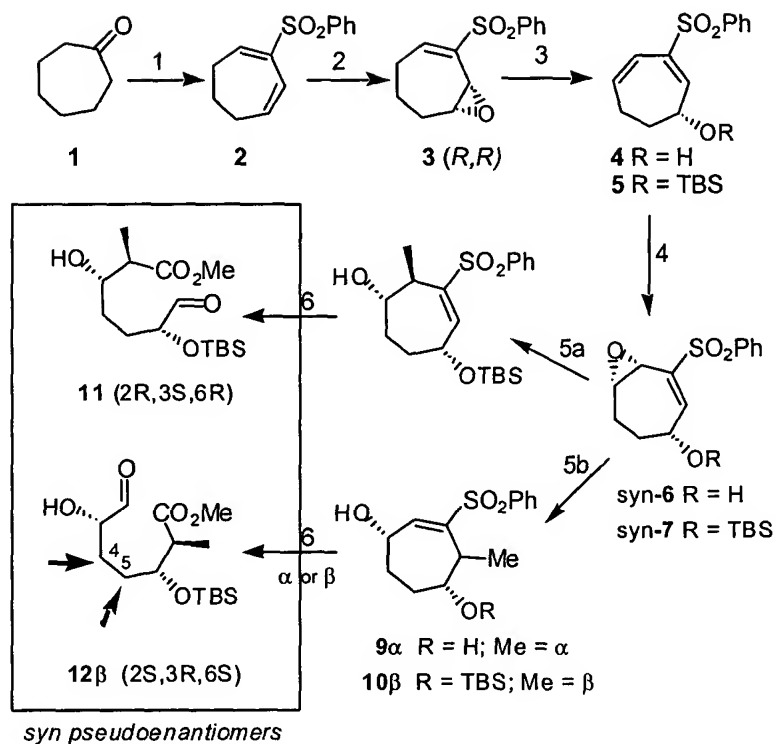
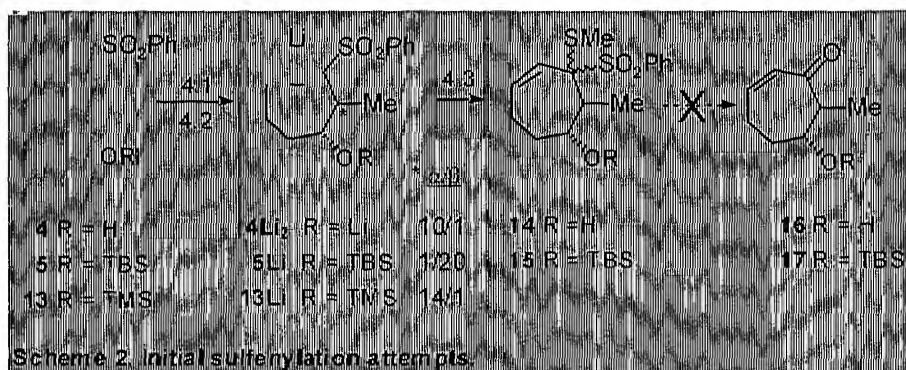


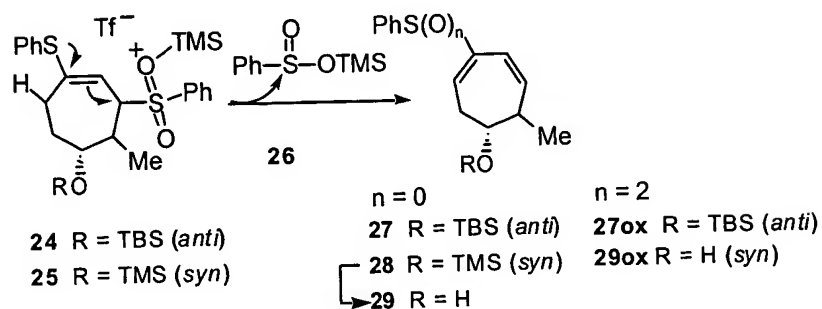
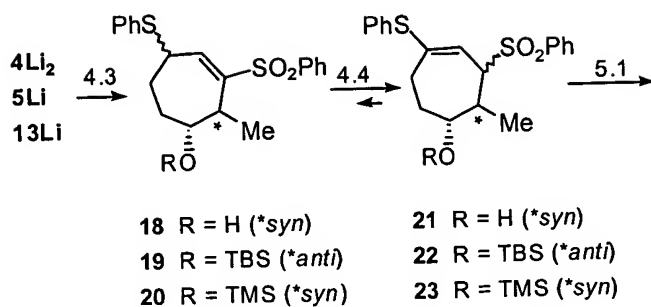
FIGURE 1



Scheme 1. Preparation of acyclic arrays

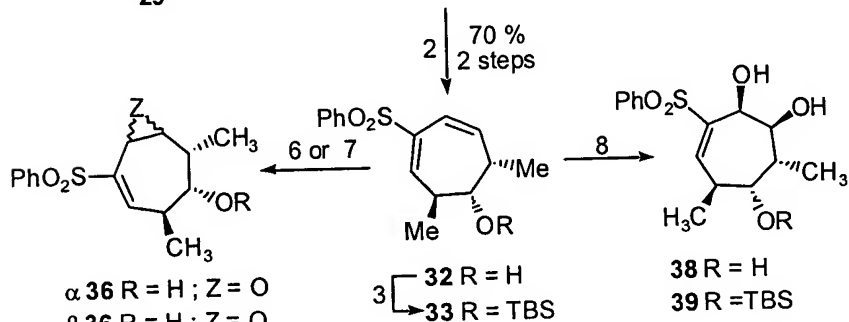
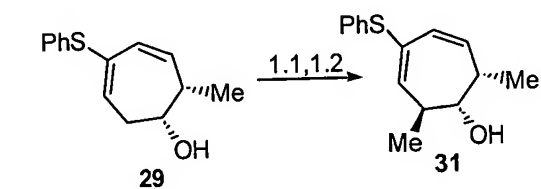
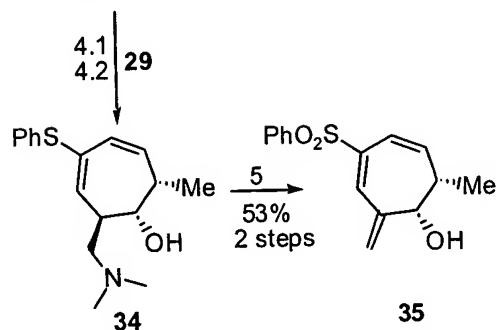
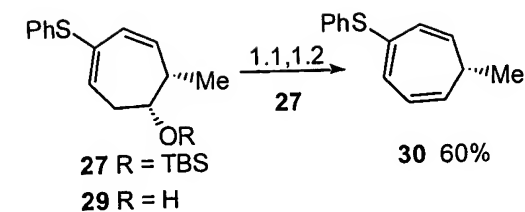


**FIGURE 2**



**Scheme 3. Novel gamma sulfonylation and diene transposition.**

FIGURE 3



$\alpha$  36 R = H ; Z = O  
 $\beta$  36 R = H ; Z = O  
 $\alpha$  37 R = TBS; Z = O  
 $\beta$  37 R = TBS; Z = O

**Scheme 4. Preparation of stereopentad progenitors.**

1.1 *n*-BuLi (2.2 eq), THF, -78°C to -7°C, 1.2 MeI (5 eq), -90°C to -50°C; 2 *m*-CPBA (2.2 eq); CH<sub>2</sub>Cl<sub>2</sub>, 25°C, 30 min; 3 TBSOTf (1.2 eq), Lutidine (2 eq). CH<sub>2</sub>Cl<sub>2</sub>, 25°C, 2h; 4.1 *n*-BuLi (2.2eq), THF, -78°C to -5°C, 90 min; 4.2 Eschenmoser's salt (2.5 eq), THF, -70°C to 0°C, 1.5 h; 5 *m*-CPBA (4 eq); CH<sub>2</sub>Cl<sub>2</sub>, 25°C, 1h; 6 TBHP + 5% Mo(CO)<sub>6</sub>, 88% >15:1  $\alpha/\beta$ ; 7 10% (*R,R*)-Mn(salen)Cl, H<sub>2</sub>O<sub>2</sub>, 1eq NH<sub>4</sub>OAc, 83% 1:>20  $\alpha/\beta$ , 8 OsO<sub>4</sub> cat. >80%, single diastereomer

FIGURE 4

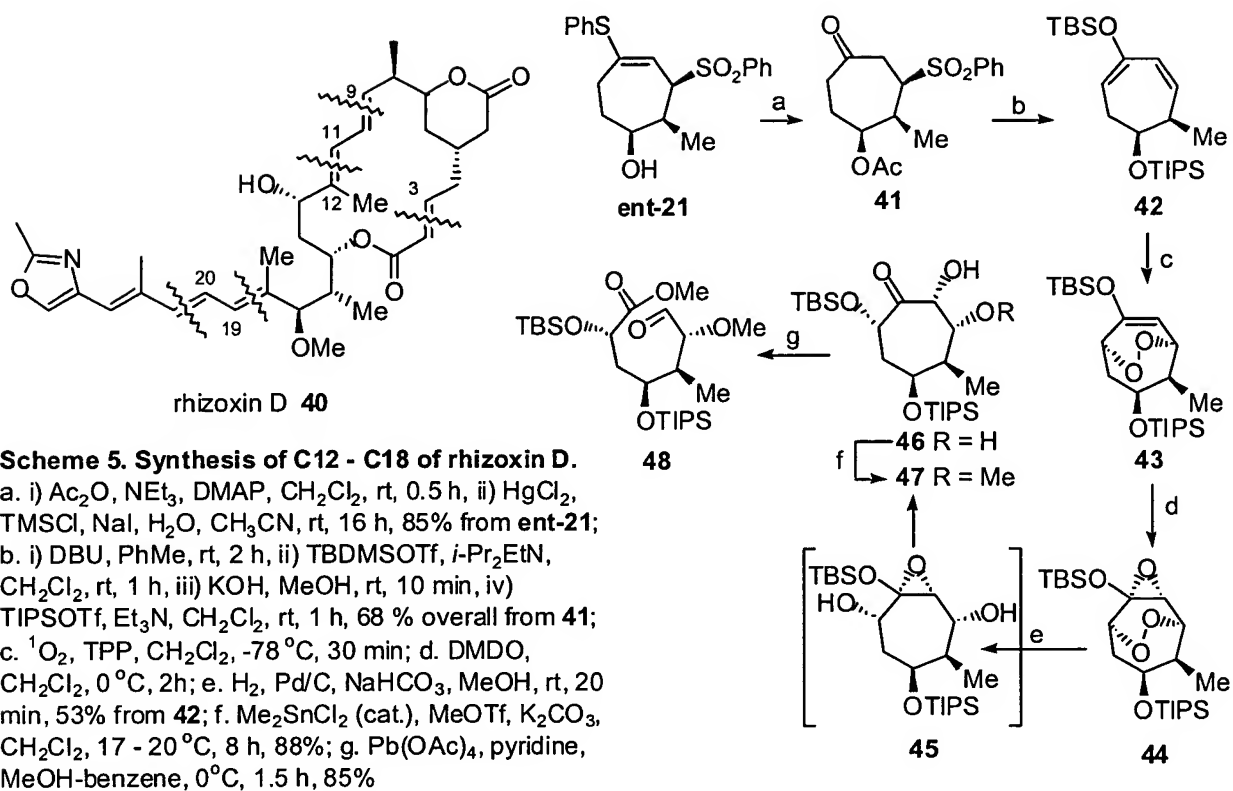
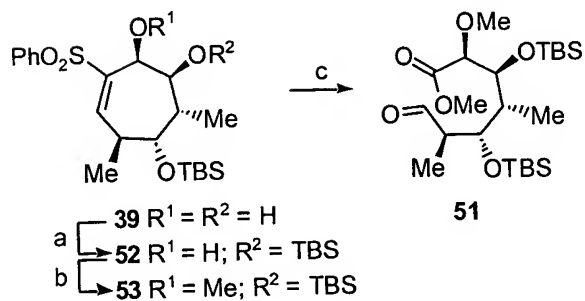
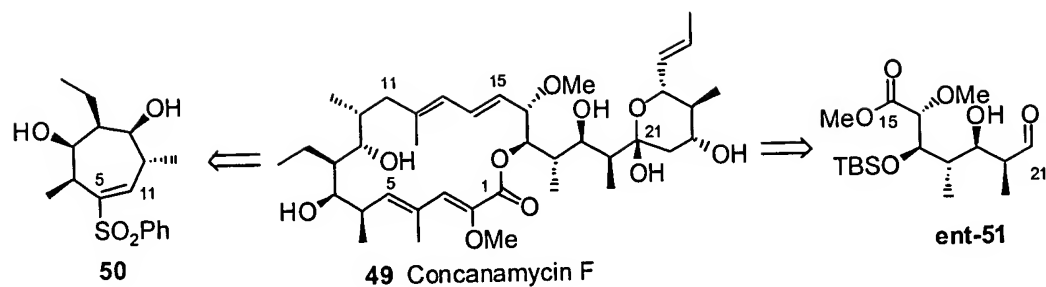


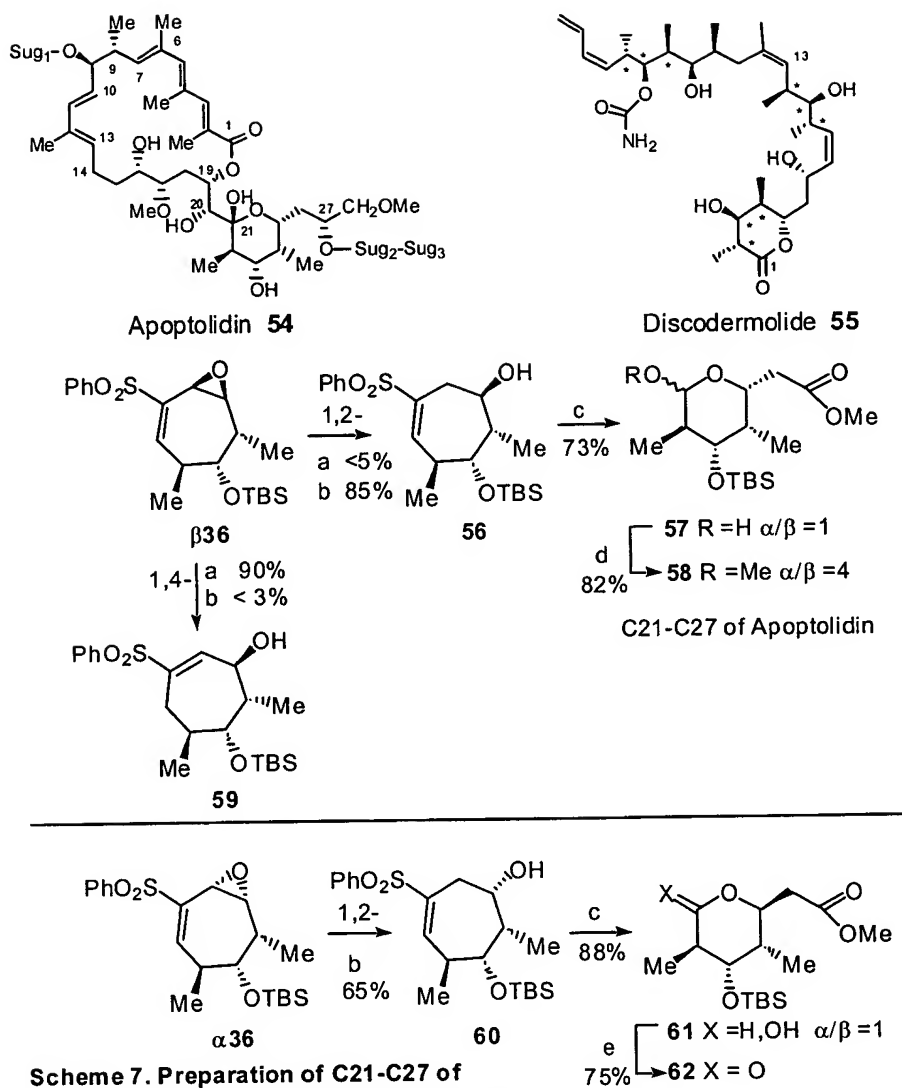
FIGURE 5



**Scheme 6. Synthesis of the ent-C15-C21 fragment of Concanamycin F.**

a TBSOTf, 2,6-Lutidine, CH<sub>2</sub>Cl<sub>2</sub>, -78°C, 24h, 99% ; b KOH/Mel/DMSO, 25°C, 5 min; 94%; c O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeOH (1:2), NaHCO<sub>3</sub>, -78°C, 5 min, then PPh<sub>3</sub>, 92%

FIGURE 6



**Scheme 7. Preparation of C21-C27 of Apoptolidin and C1-C7 of Discodermolide.**

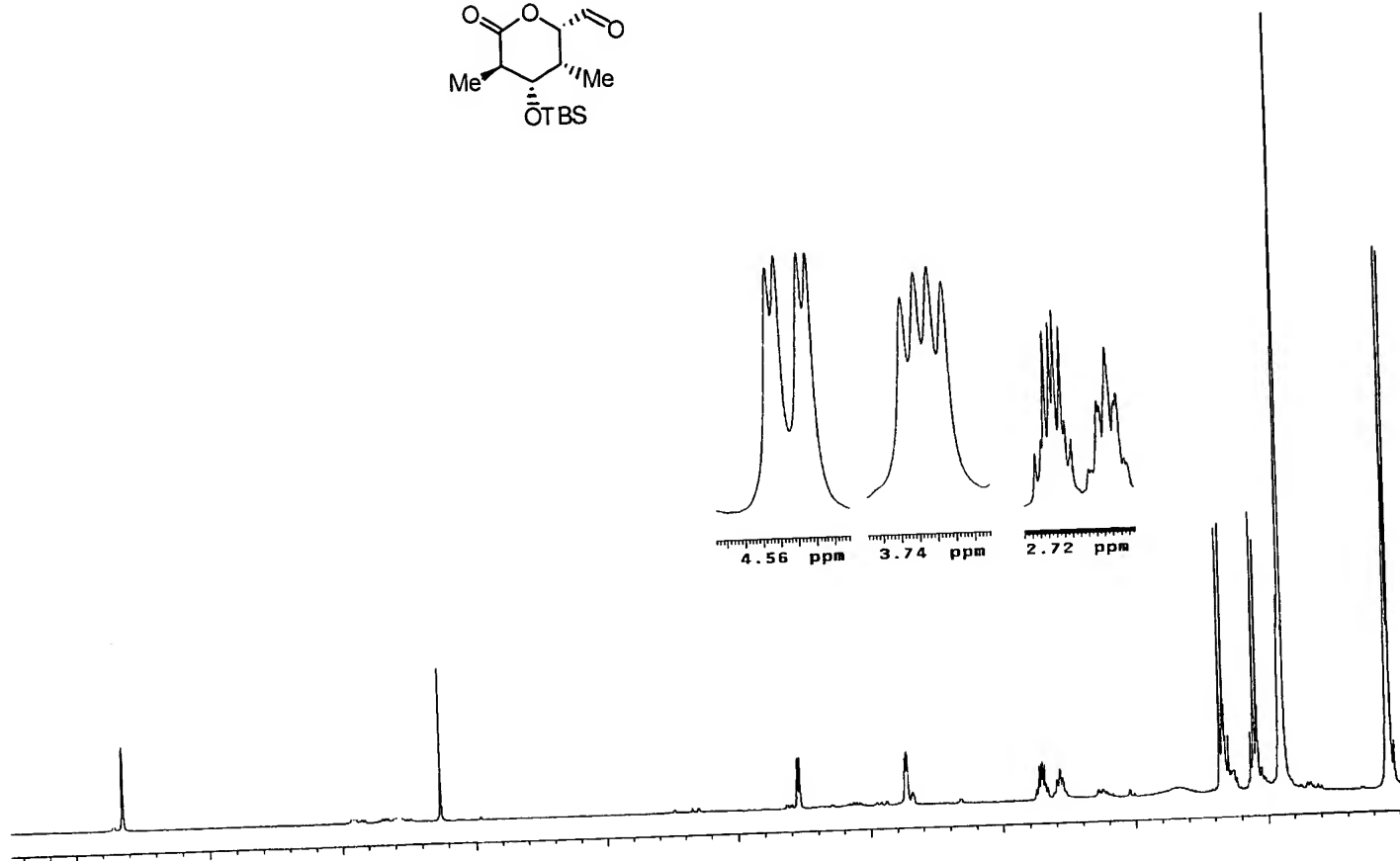
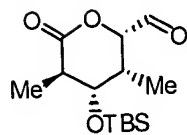
a  $\text{BH}_3 \cdot \text{THF}$  (1.6 eq), THF,  $0^\circ\text{C}$ , warm to  $25^\circ\text{C}$ , 12 h;  
 b 1.5 eq DIBAL-H,  $-78^\circ\text{C}$ ; c  $\text{O}_3$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1:2),  $\text{NaHCO}_3$ ,  $-78^\circ\text{C}$ , 5 min; d  $\text{Ag}_2\text{O}$ , MeI,  $\text{CH}_3\text{CN}$ , reflux, 3h; e PDC (5 eq),  $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ , 10 h

FIGURE 7

Figure 1. Evaluation and importance of the sulfur atom for this synthesis.



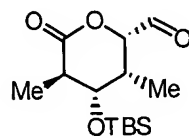
FIGURE 8 (99 Spectra)



300MHz  $^1\text{H}$  NMR of compound 22 in  $\text{CDCl}_3$

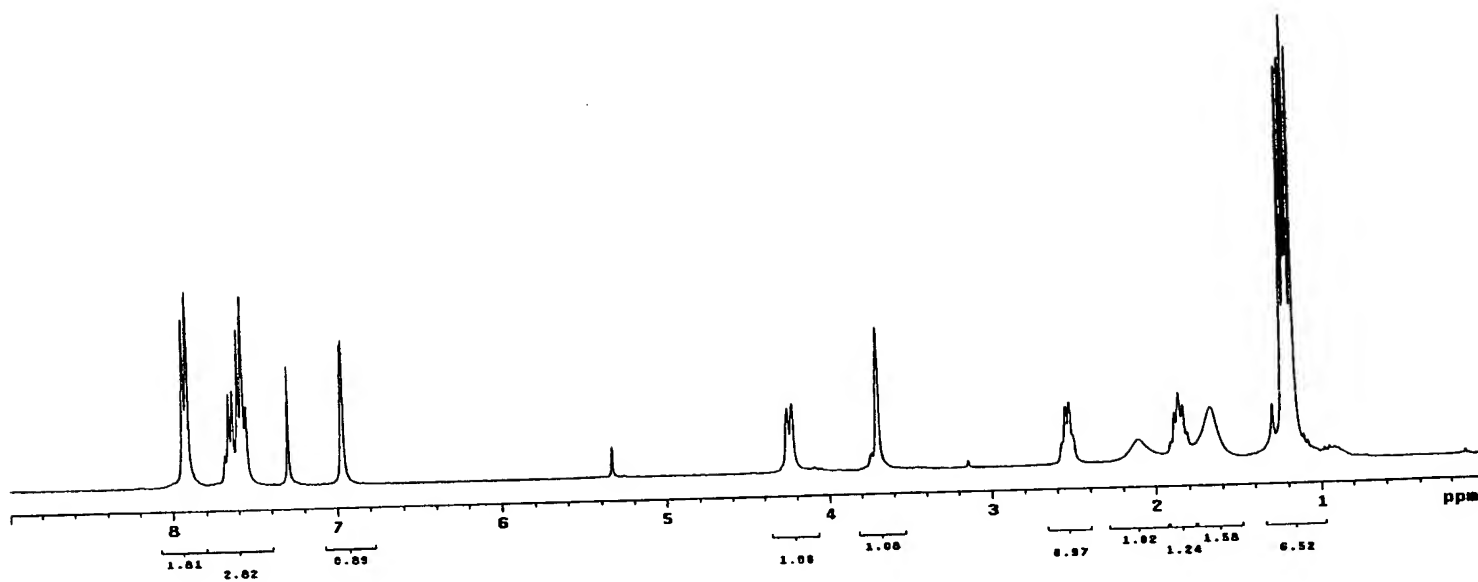
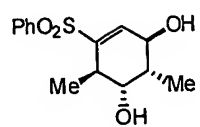


**FIGURE 8 (Cont'd)**



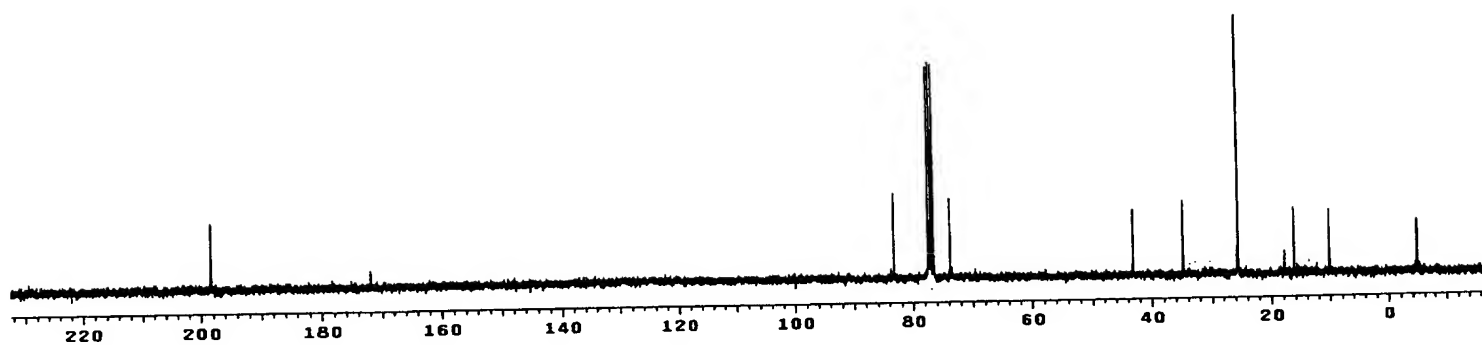
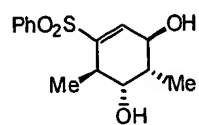
75MHz  $^{13}\text{C}$  NMR of compound **22** in  $\text{CDCl}_3$

—



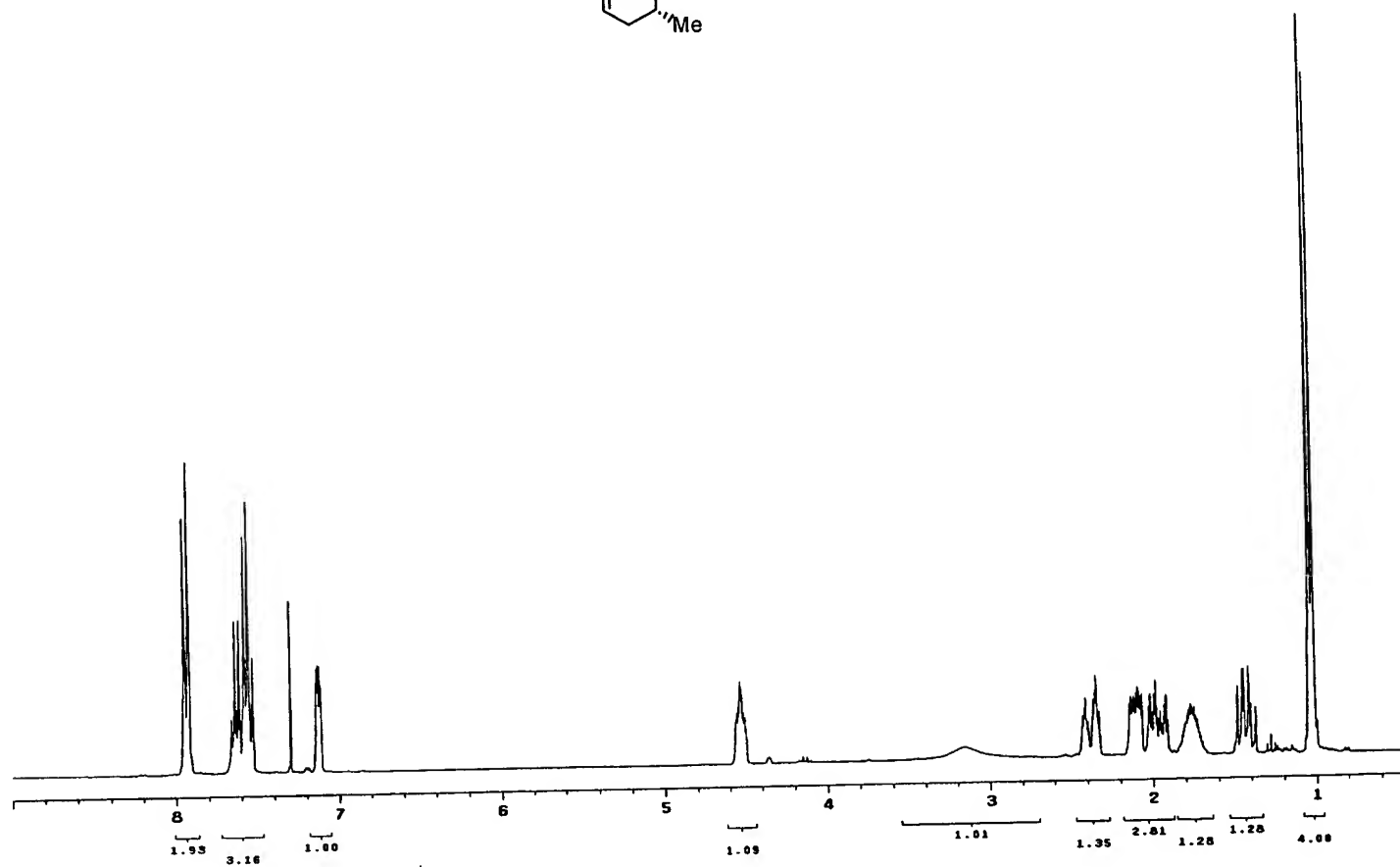
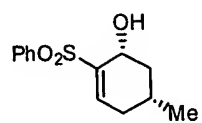
300MHz  $^1\text{H}$  NMR of compound **23** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



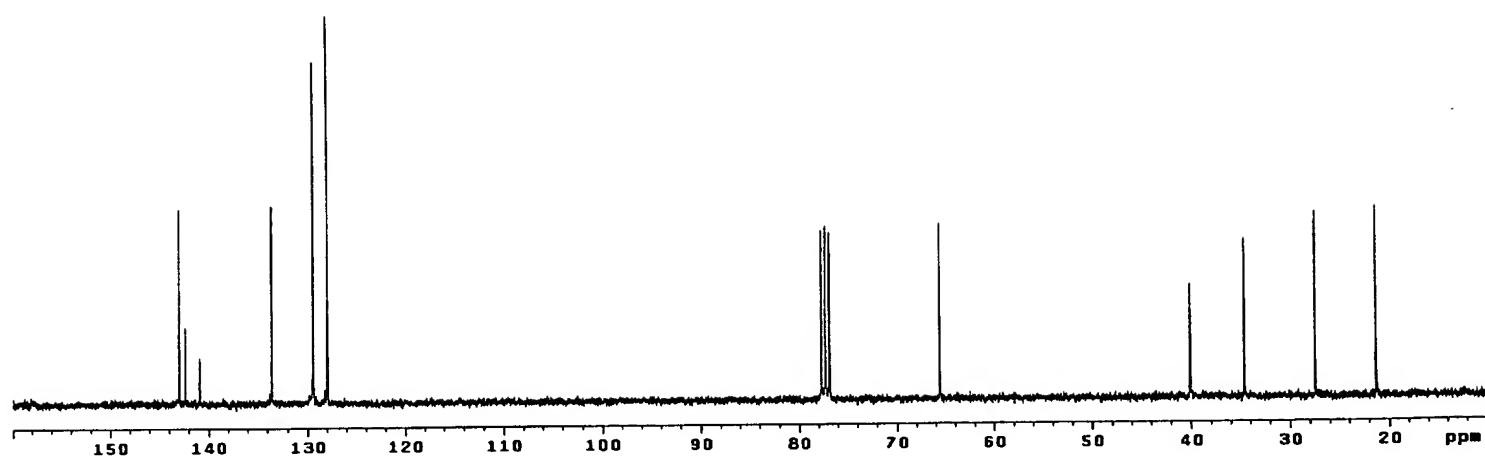
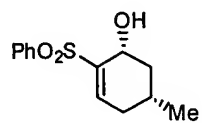
75MHz <sup>13</sup>C NMR of compound 23 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



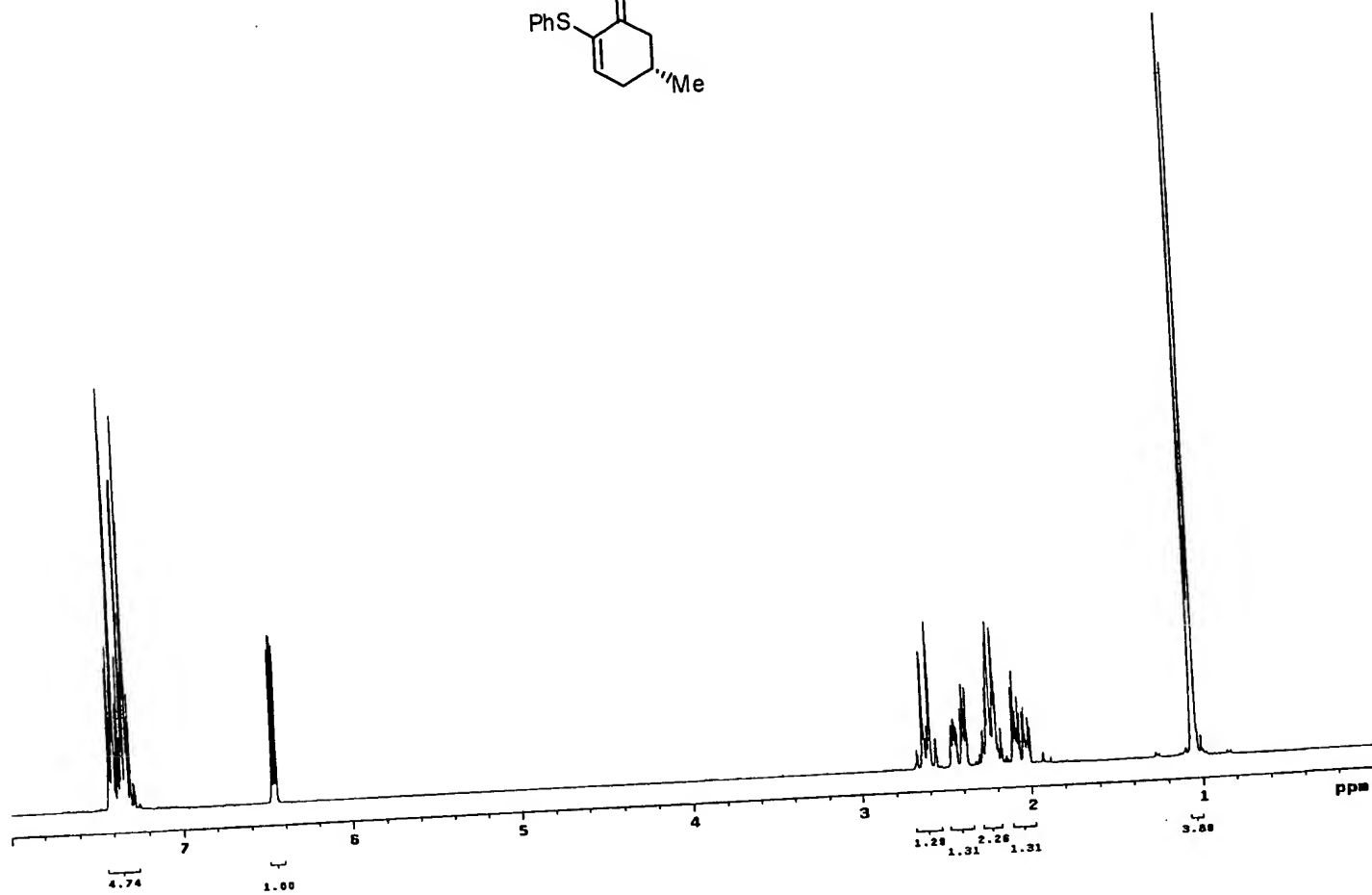
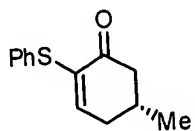
300MHz <sup>1</sup>H NMR of compound 24 in CDCl<sub>3</sub>

**FIGURE 8 (Cont'd)**



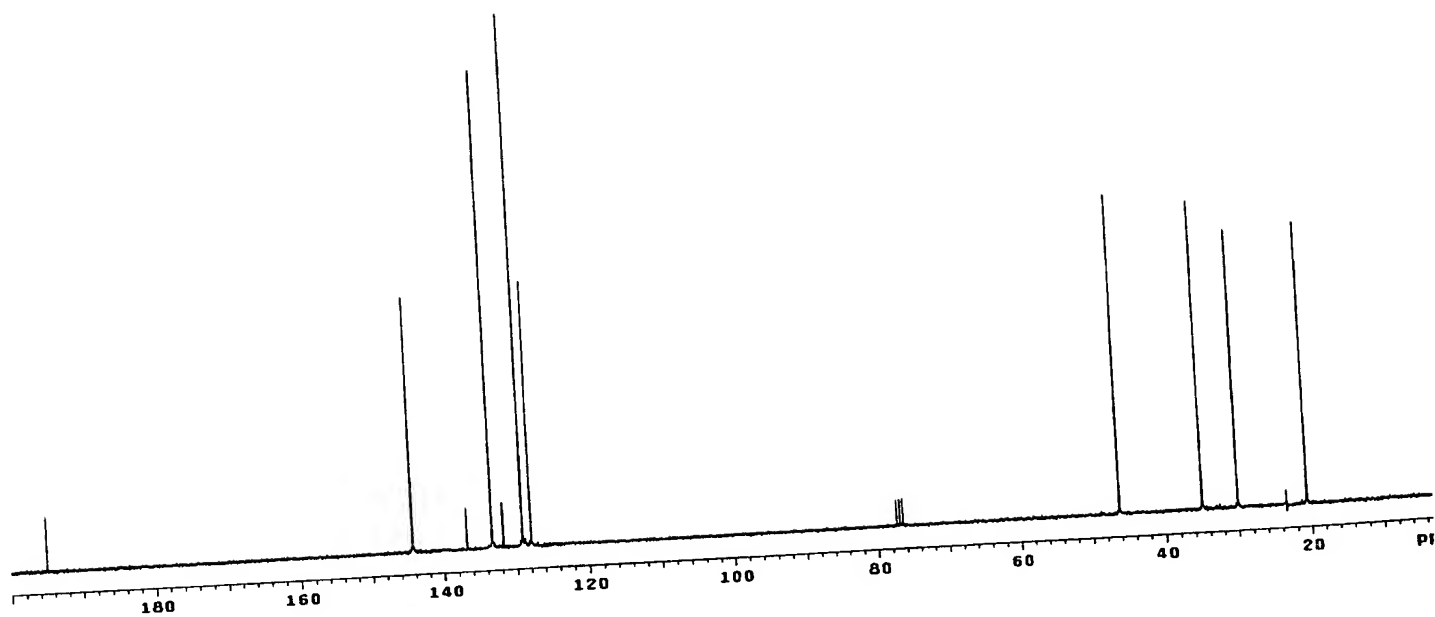
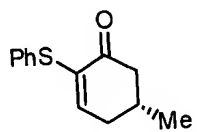
75MHz  $^{13}\text{C}$  NMR of compound **24** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



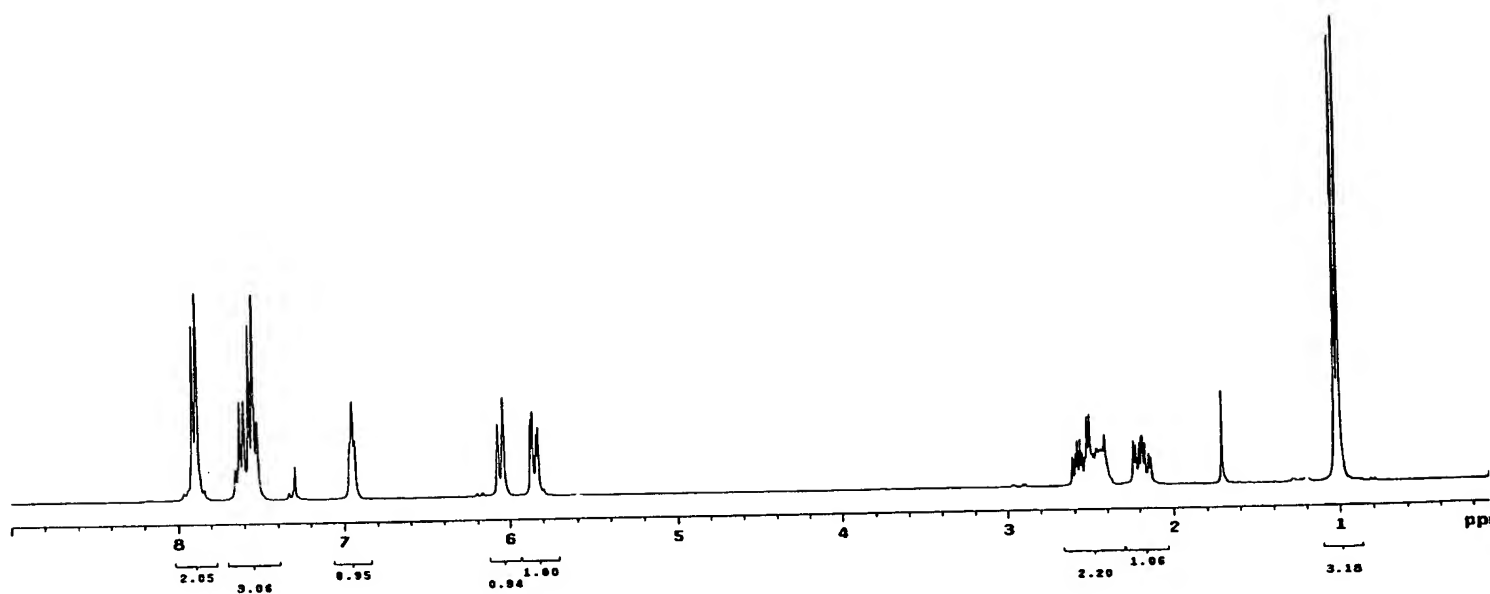
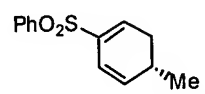
300MHz  $^1\text{H}$  NMR of compound 28 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 28 in  $\text{CDCl}_3$

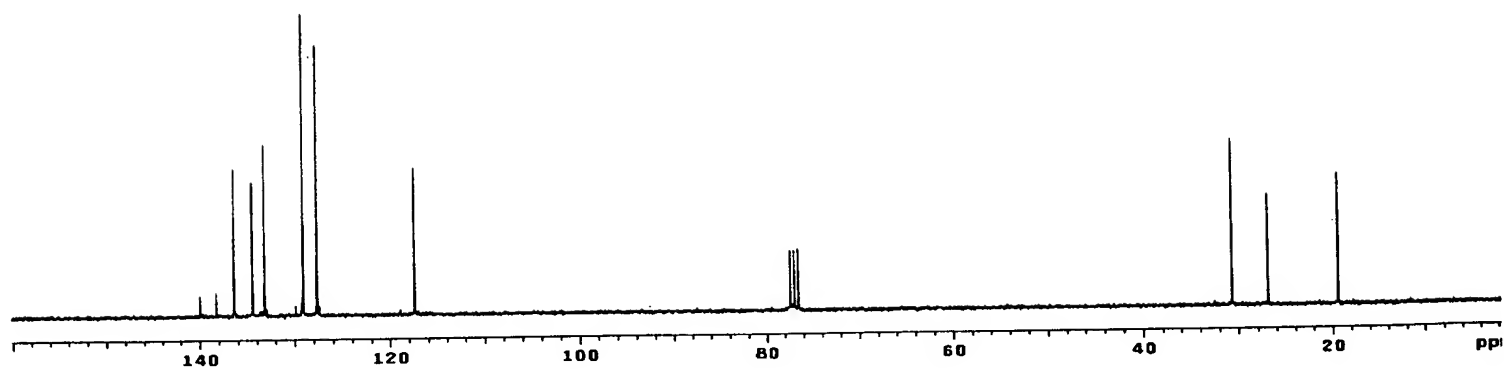
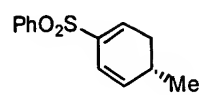
FIGURE 8 (Cont'd)



300MHz <sup>1</sup>H NMR of compound 29 in CDCl<sub>3</sub>

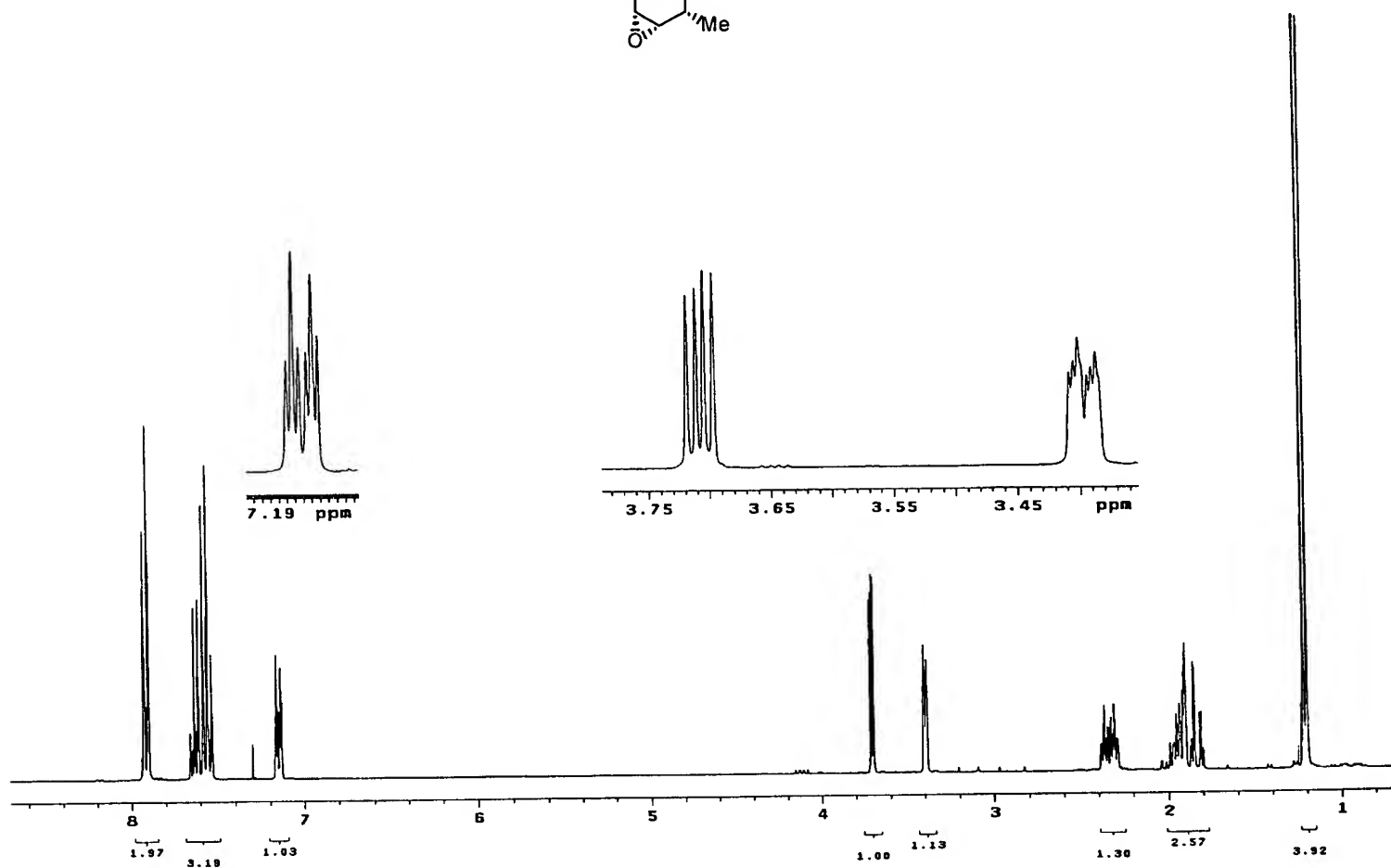
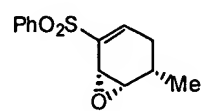


**FIGURE 8 (Cont'd)**



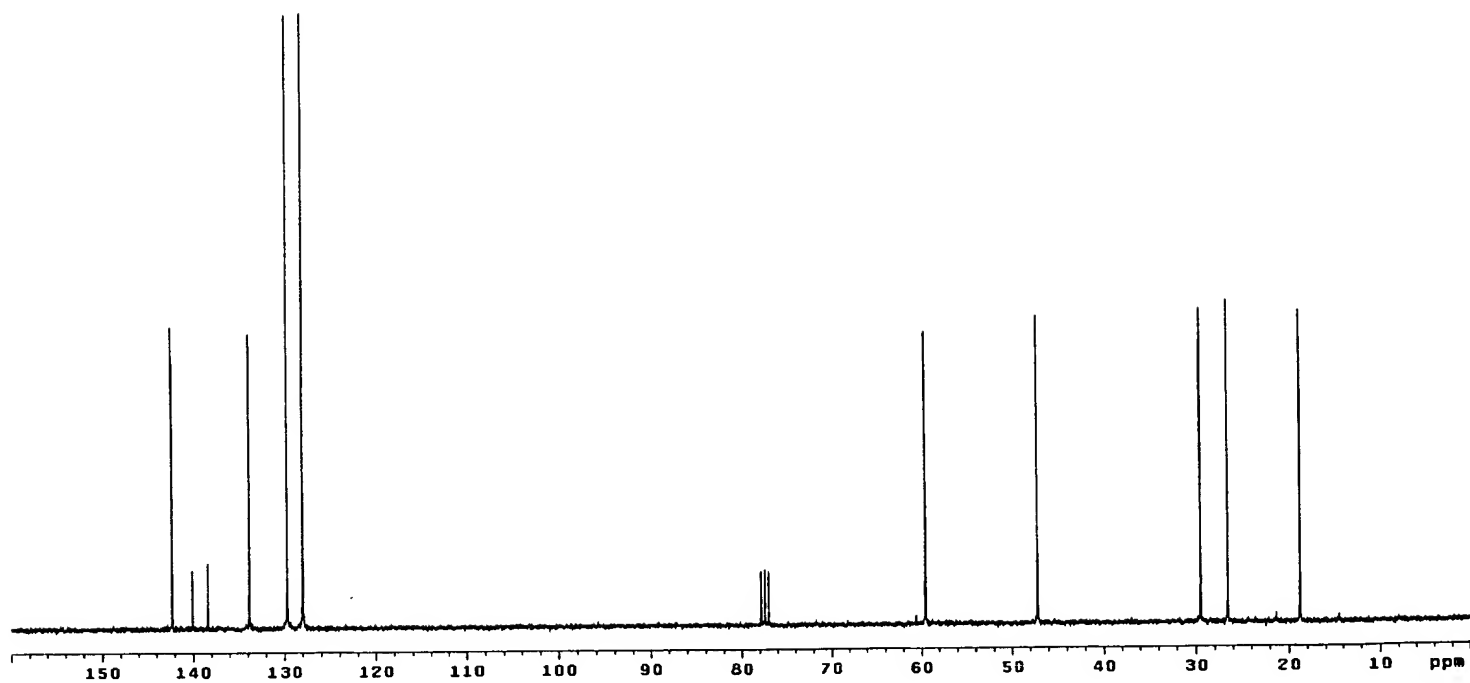
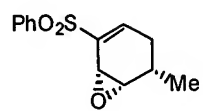
75MHz  $^{13}\text{C}$  NMR of compound **29** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



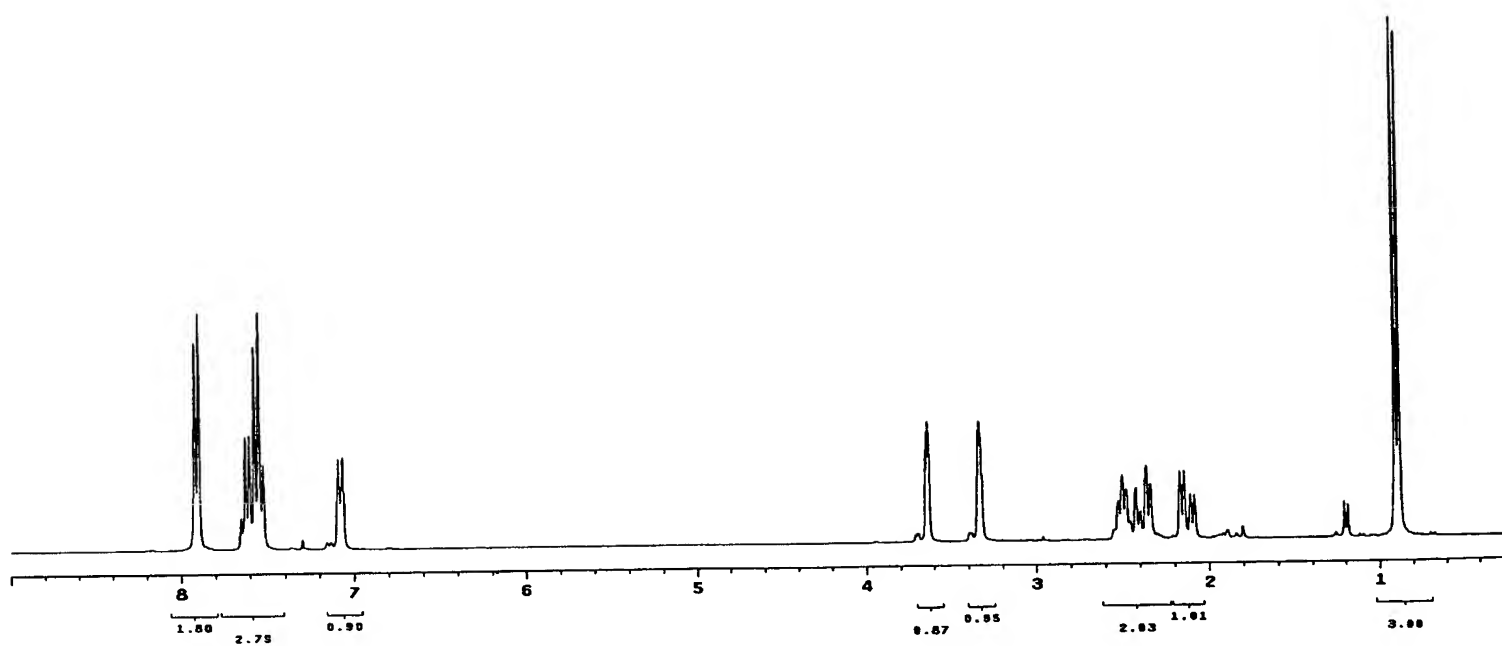
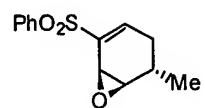
300MHz  $^1\text{H}$  NMR of compound **30** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



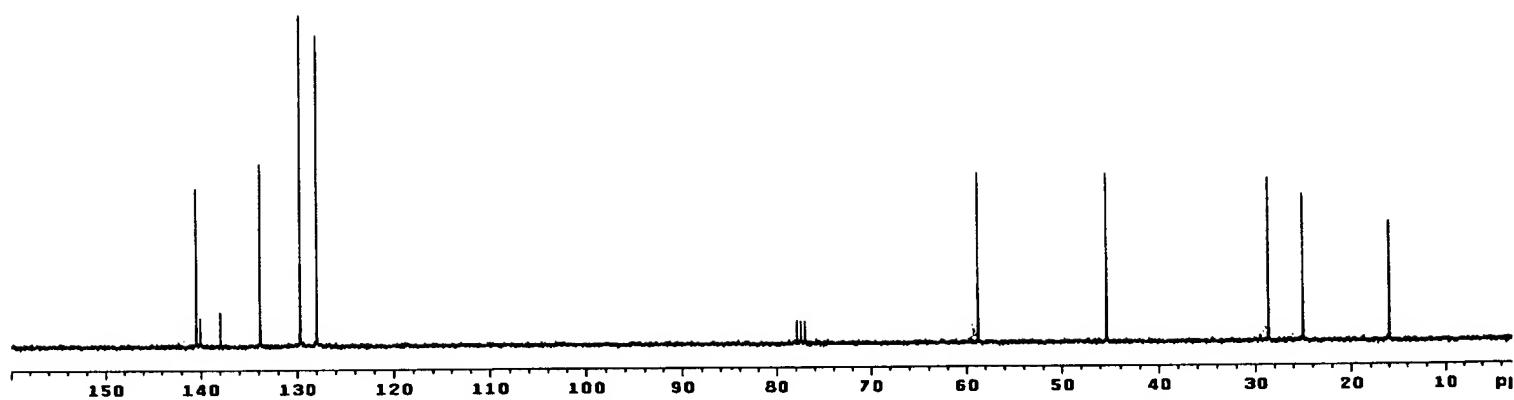
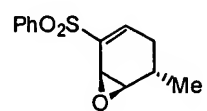
75MHz <sup>13</sup>C NMR of compound **30** in CDCl<sub>3</sub>

**FIGURE 8 (Cont'd)**



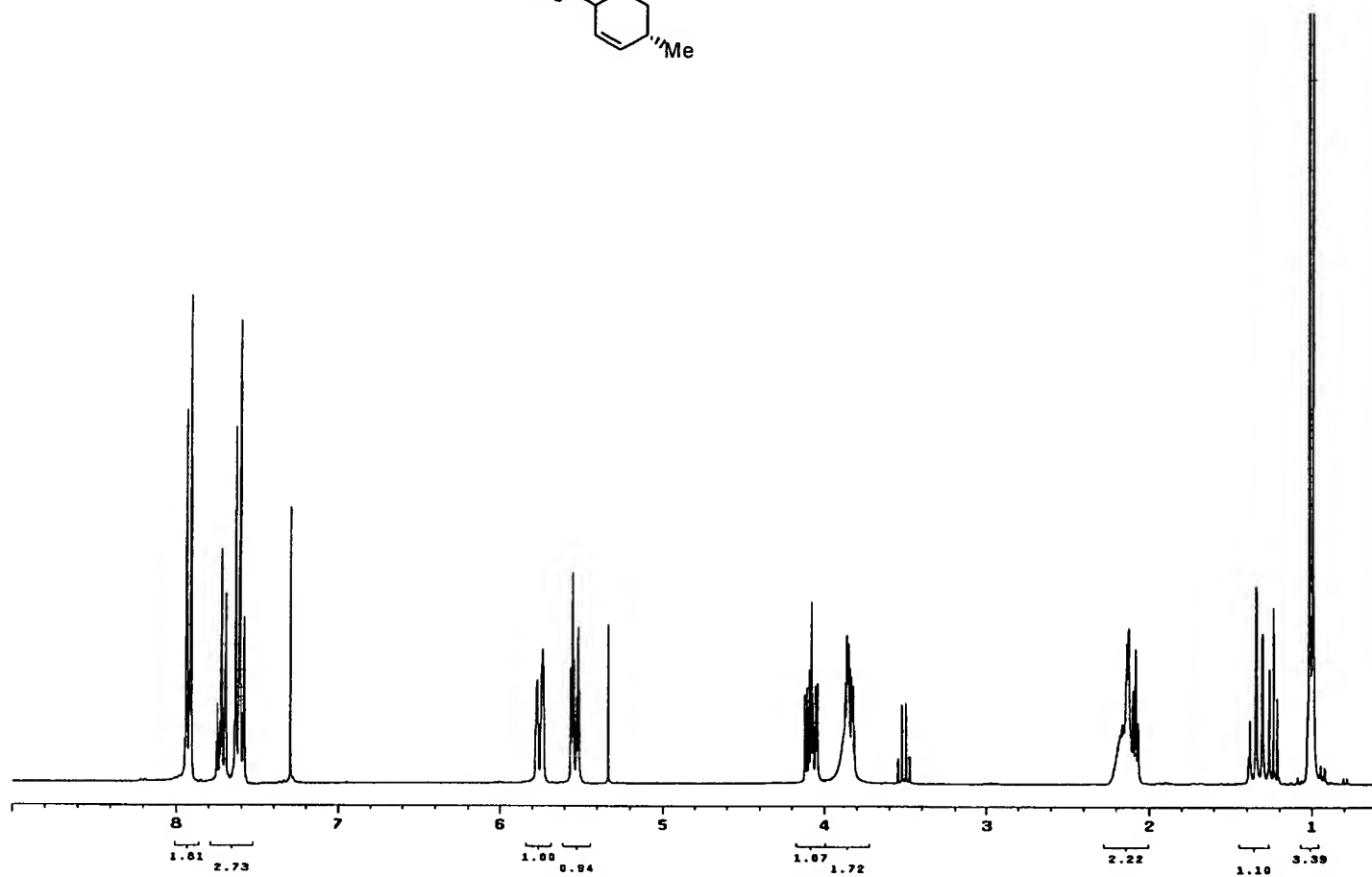
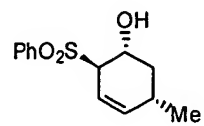
300MHz <sup>1</sup>H NMR of compound **31** in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



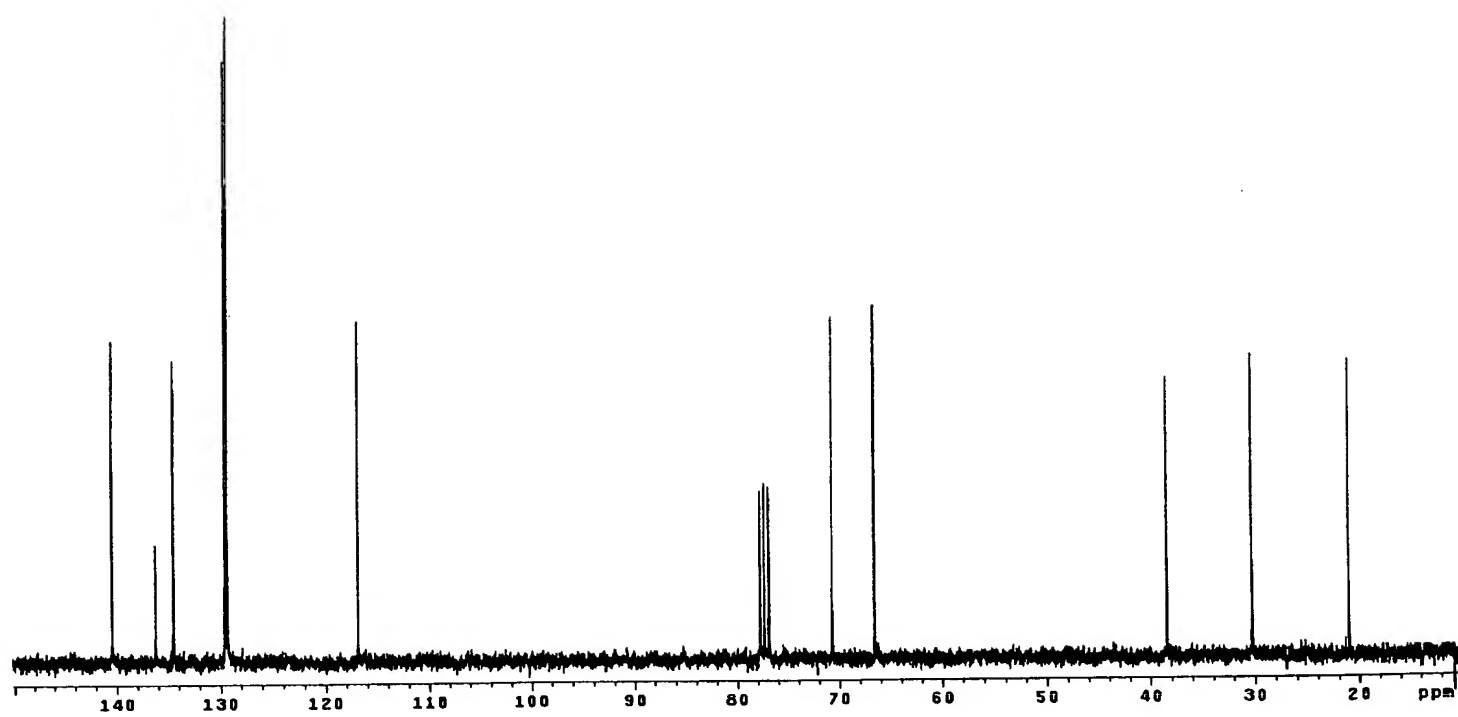
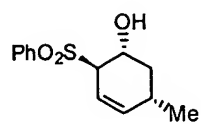
75MHz  $^{13}\text{C}$  NMR of compound **31** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



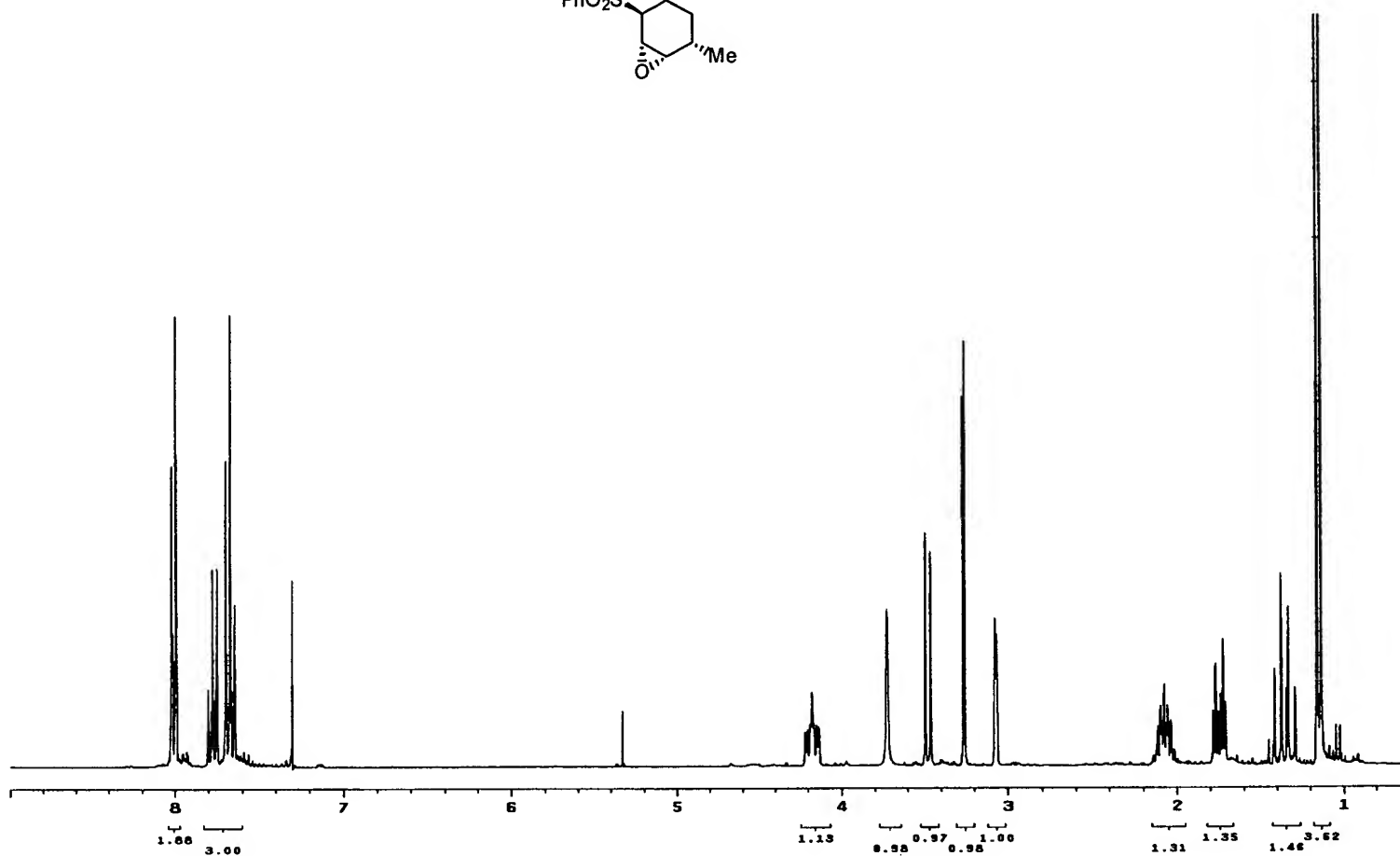
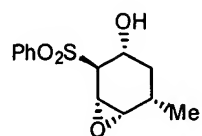
300MHz <sup>1</sup>H NMR of compound 32 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound **32** in  $\text{CDCl}_3$

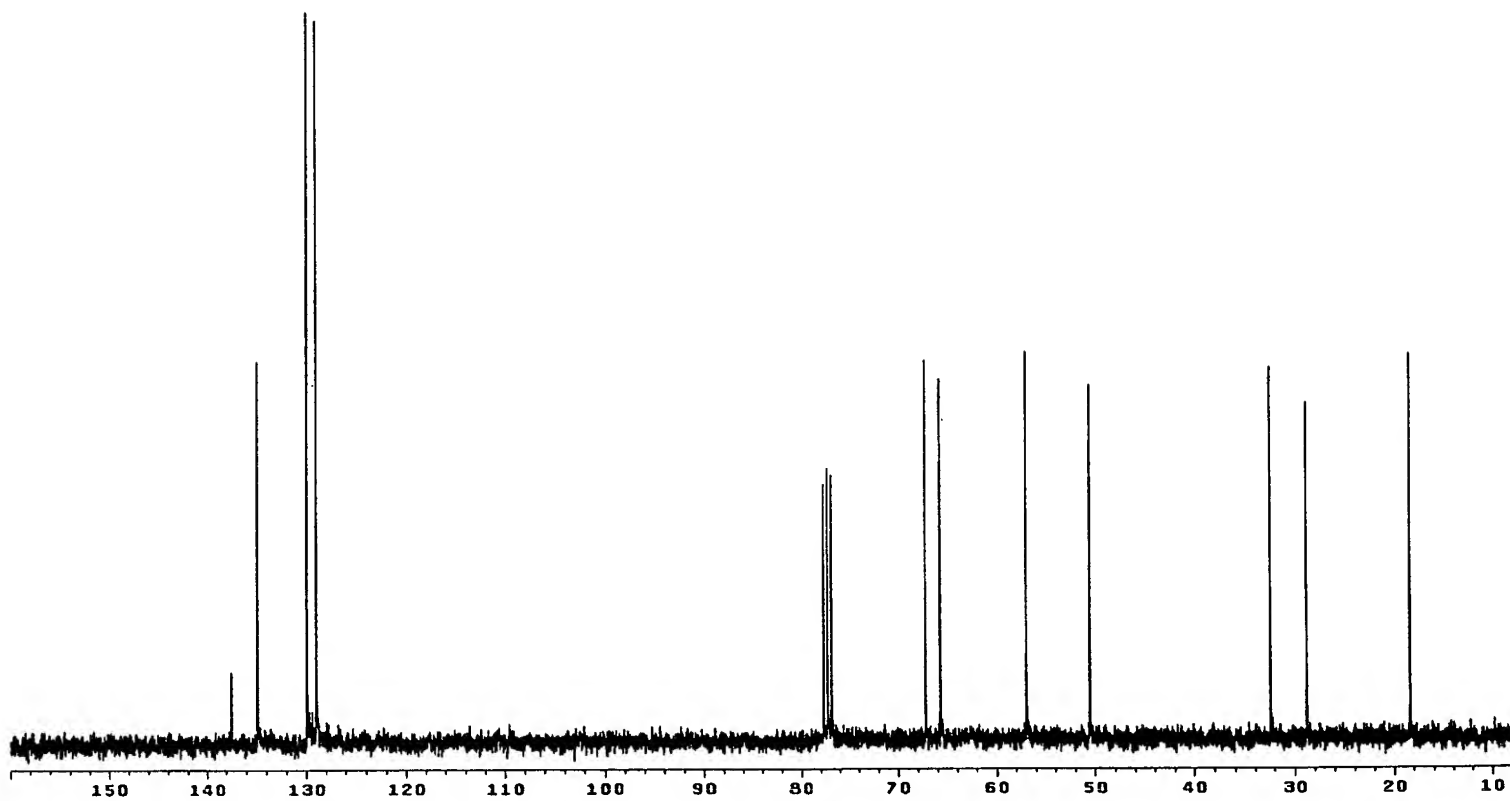
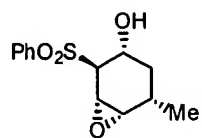
FIGURE 8 (Cont'd)



300MHz <sup>1</sup>H NMR of compound 33 in CDCl<sub>3</sub>

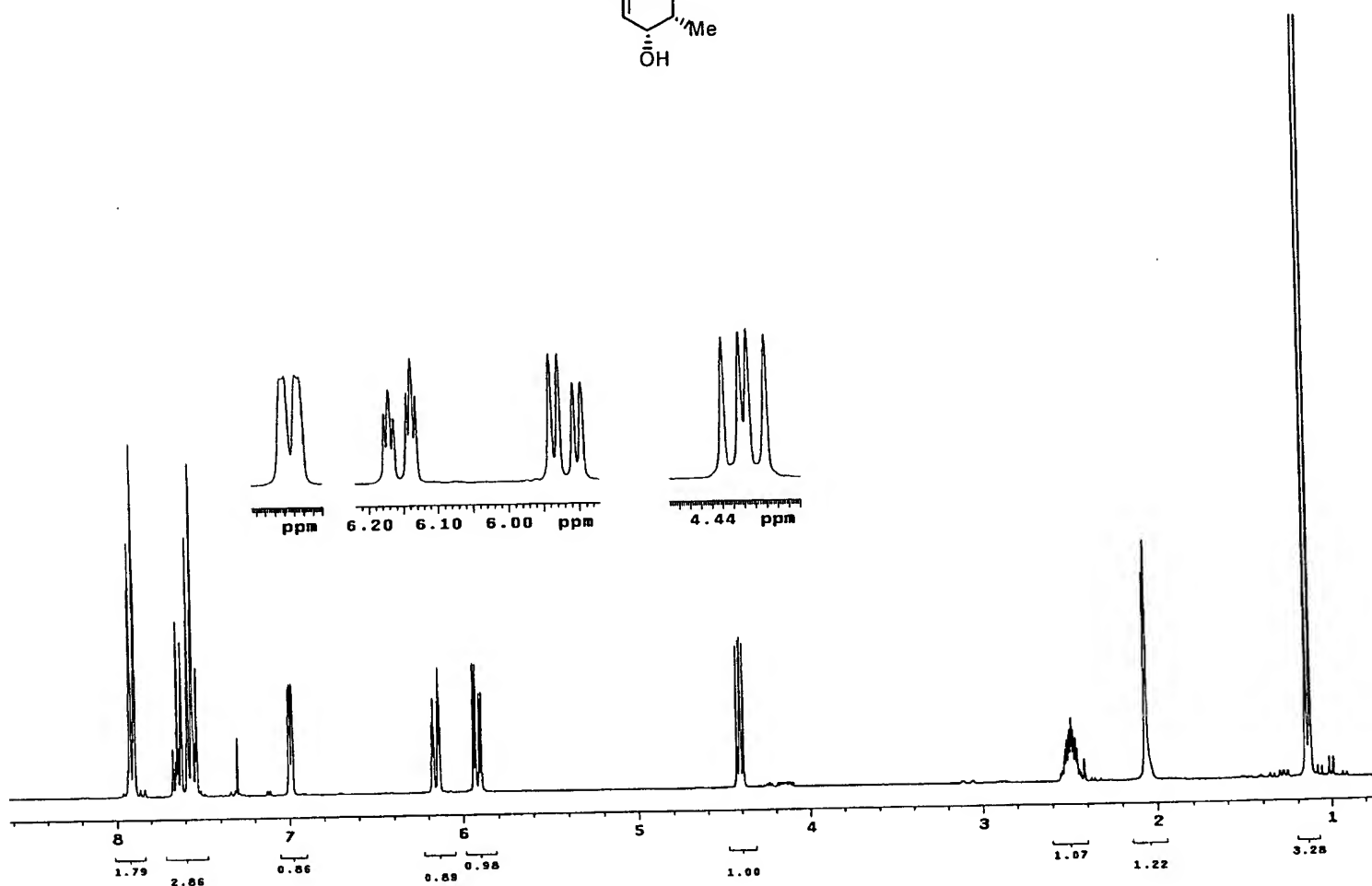
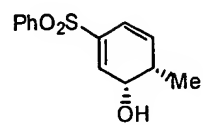


FIGURE 8 (Cont'd)



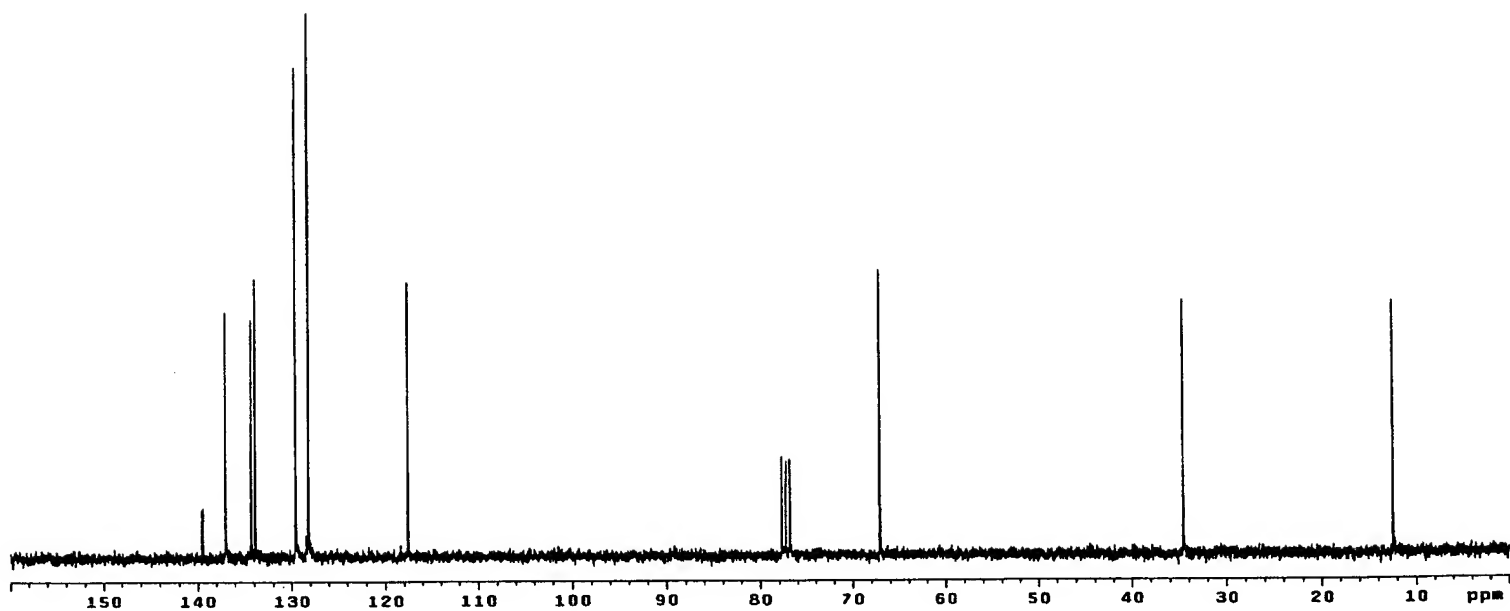
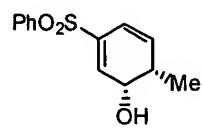
75MHz <sup>13</sup>C NMR of compound 33 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



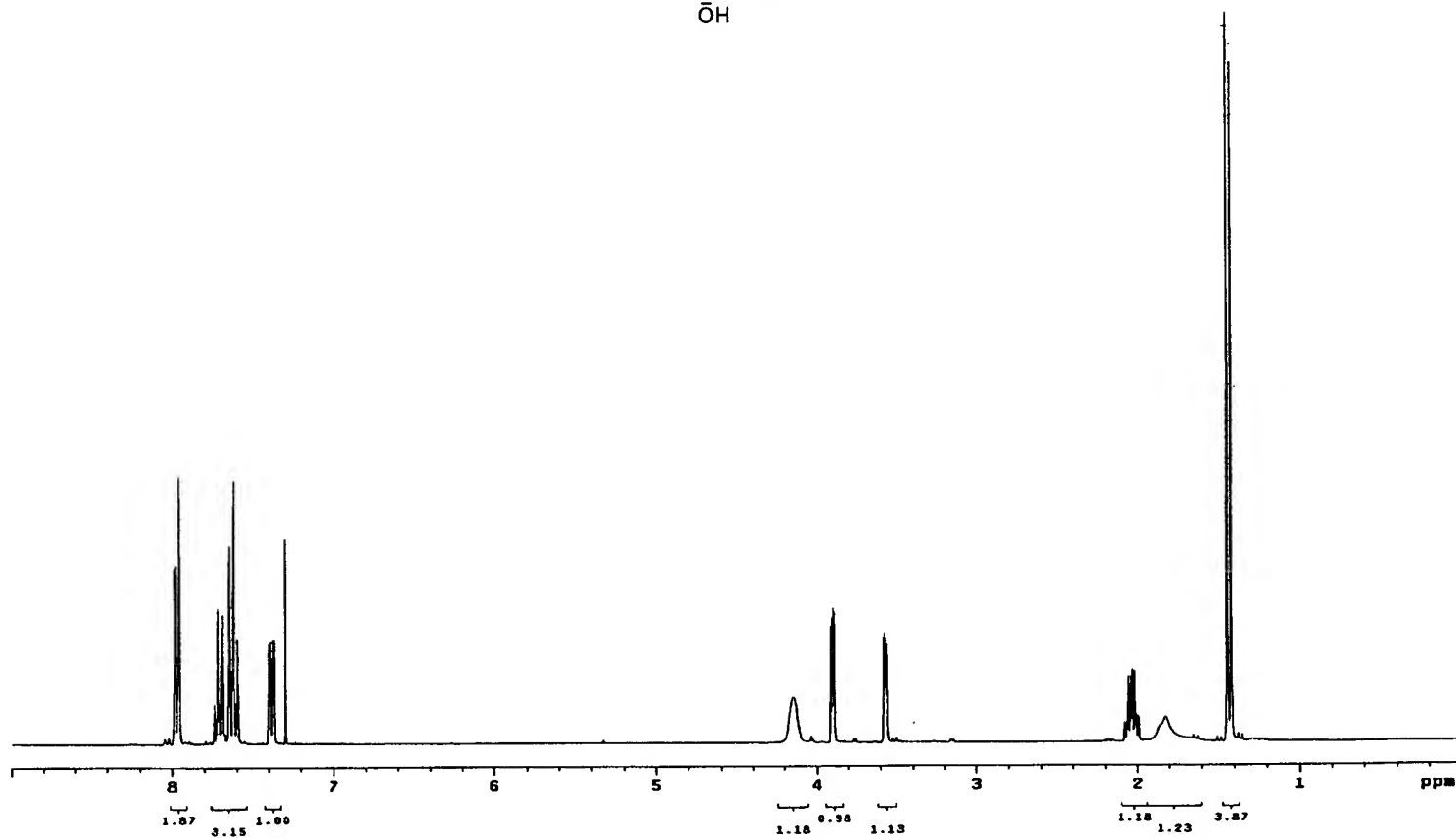
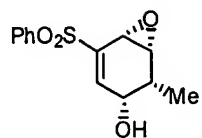
300MHz <sup>1</sup>H NMR of compound 35 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



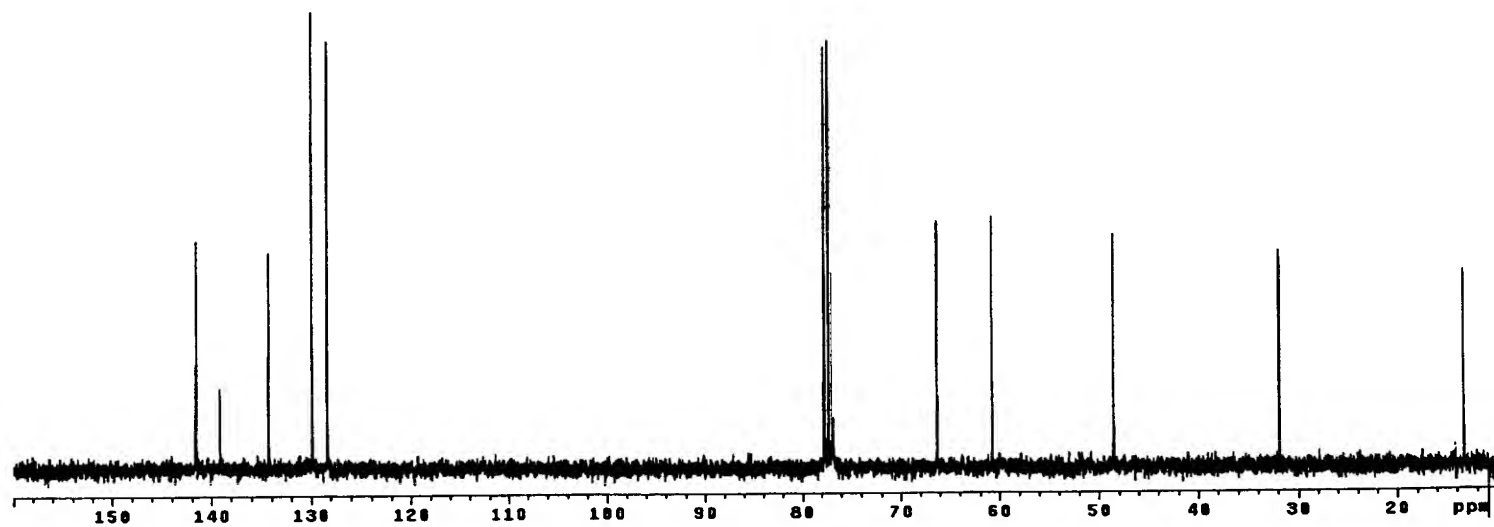
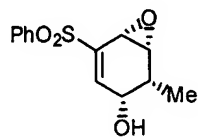
75MHz  $^{13}\text{C}$  NMR of compound 35 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



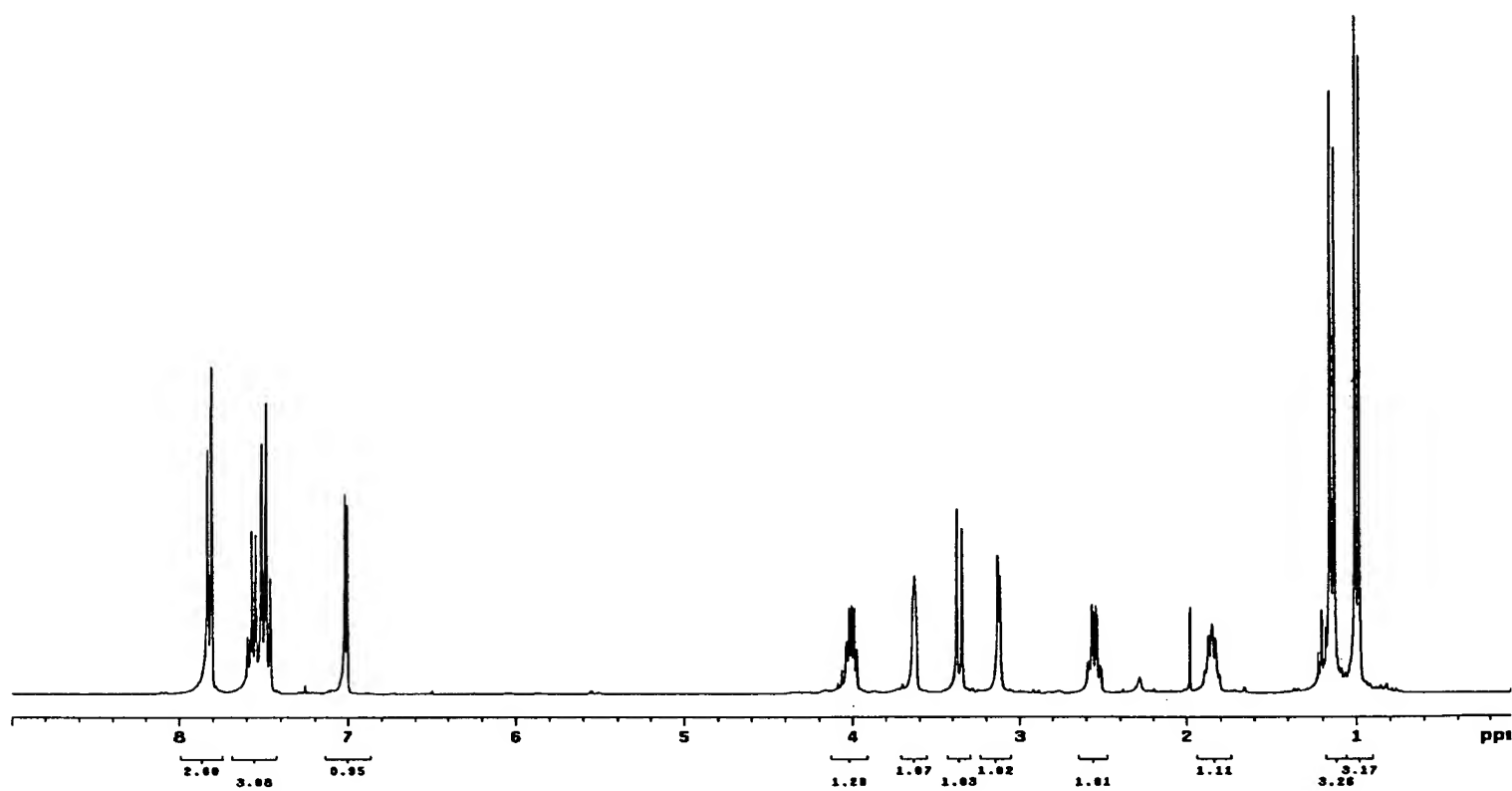
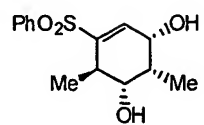
300MHz  $^1\text{H}$  NMR of compound 36 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



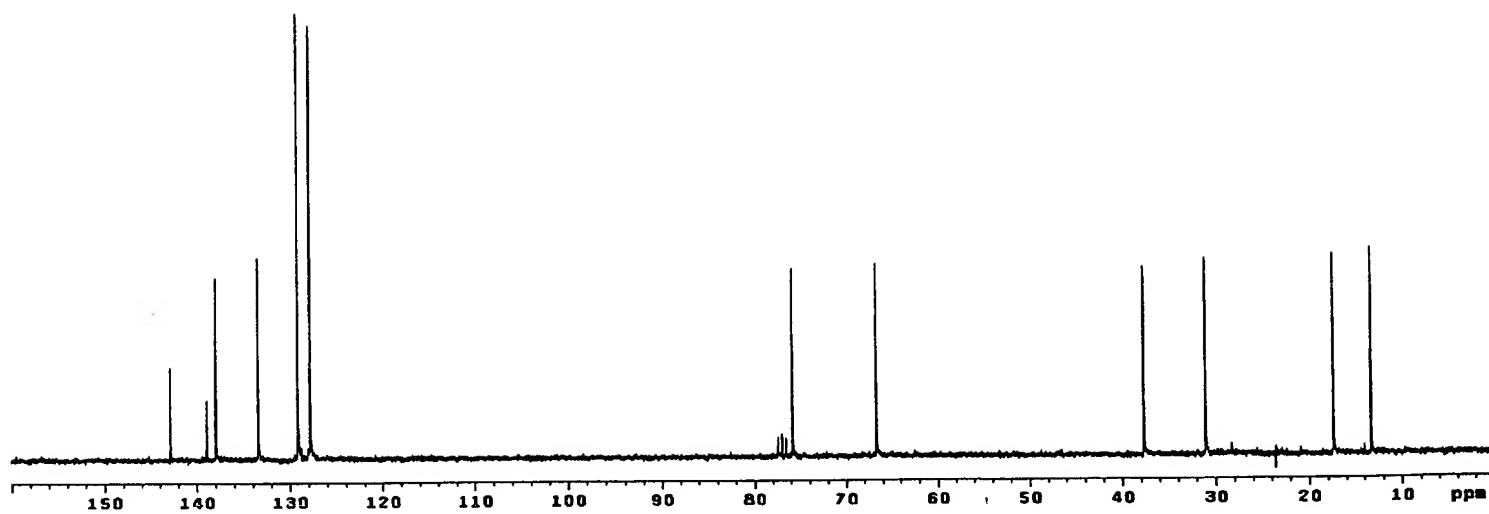
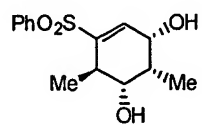
75MHz <sup>13</sup>C NMR of compound 36 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



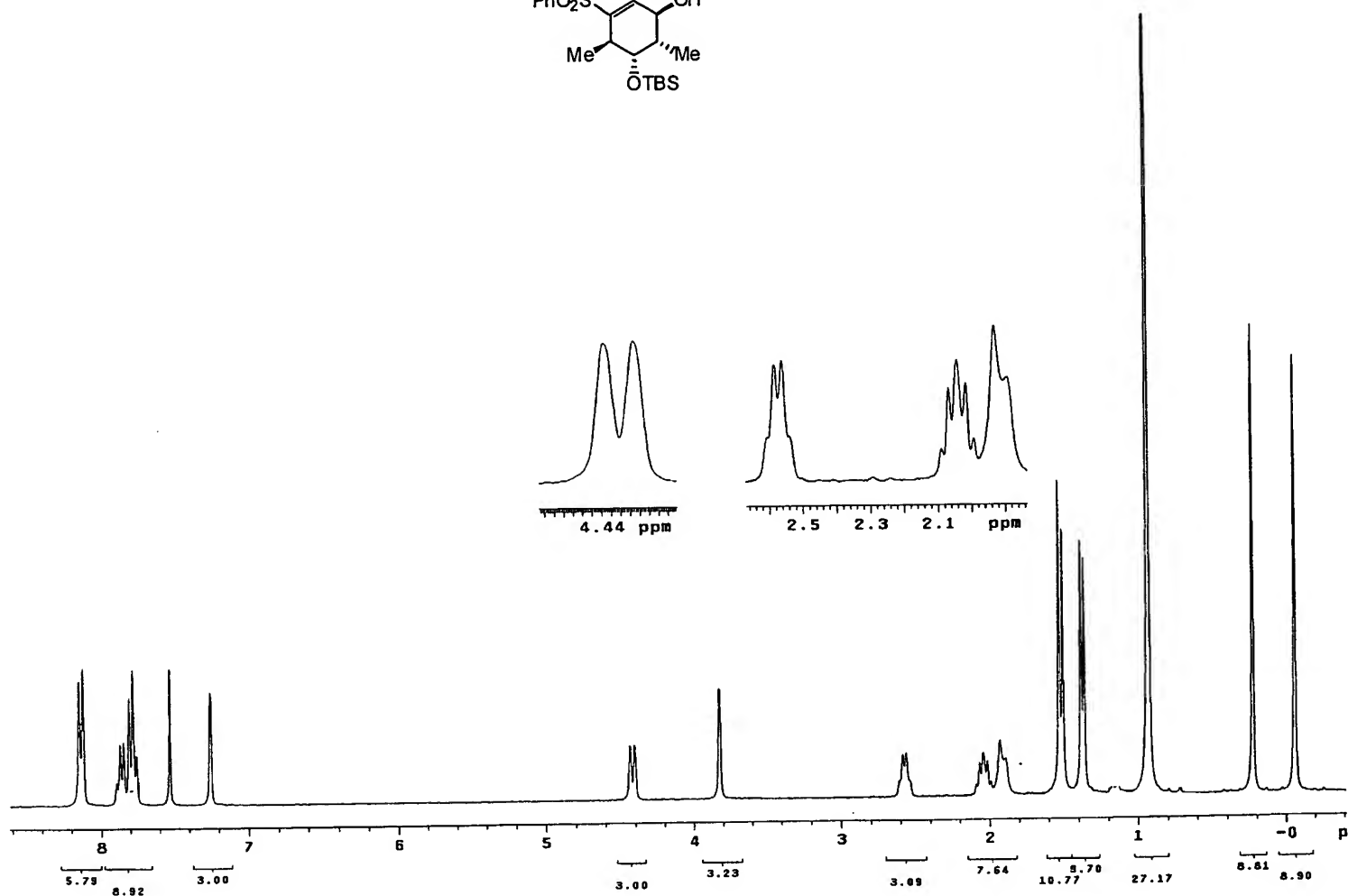
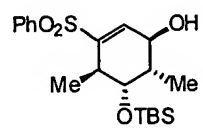
300MHz <sup>1</sup>H NMR of compound 37 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



75MHz <sup>13</sup>C NMR of compound 37 in CDCl<sub>3</sub>

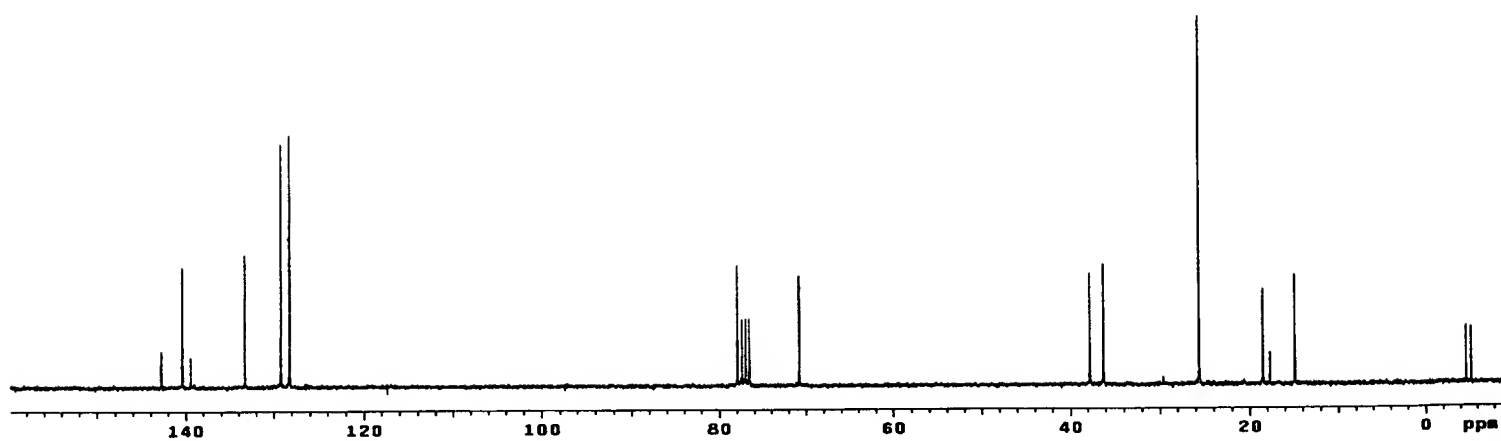
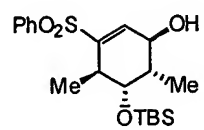
FIGURE 8 (Cont'd)



300MHz <sup>1</sup>H NMR of compound 38 in CDCl<sub>3</sub>

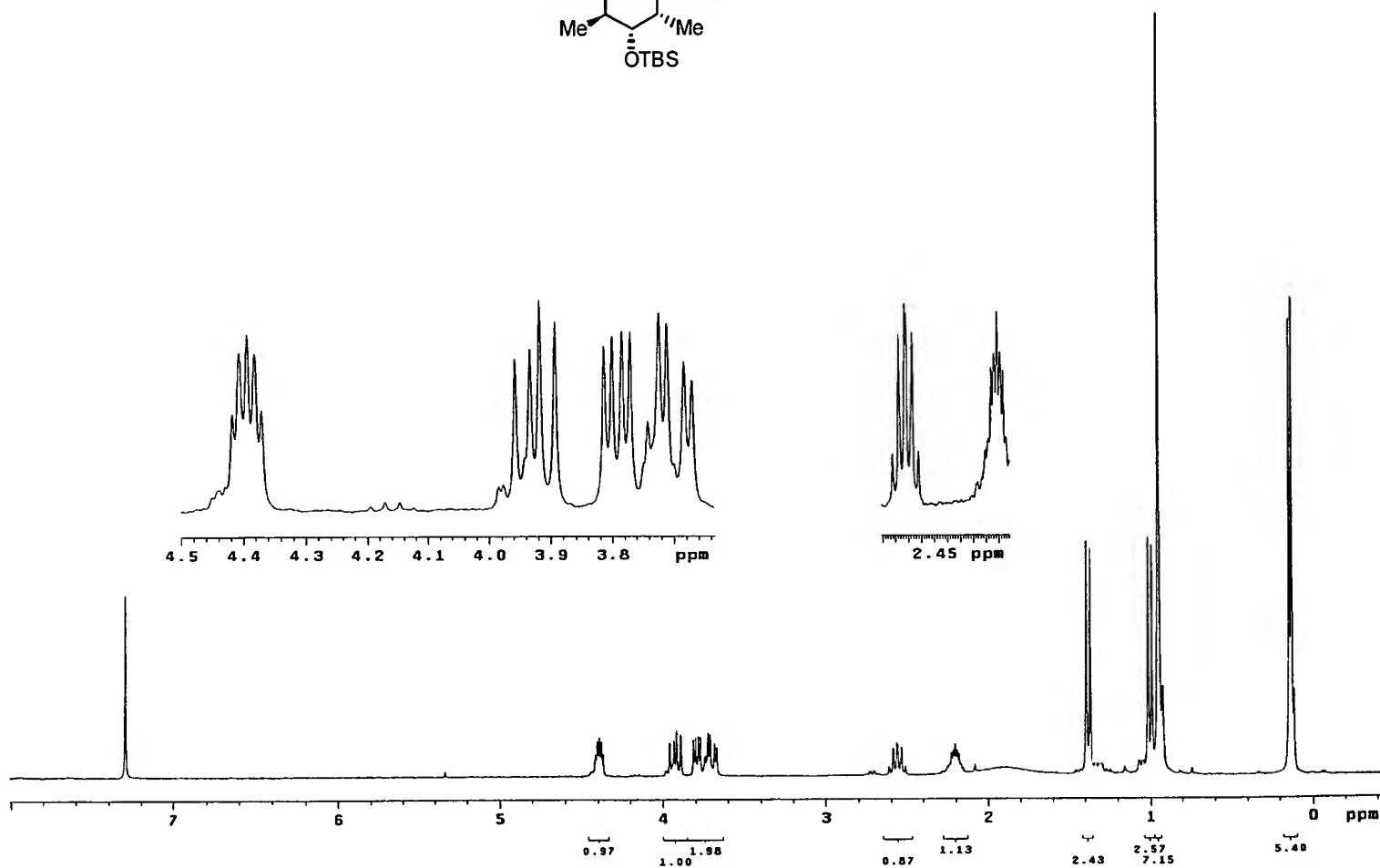
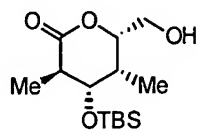


**FIGURE 8 (Cont'd)**



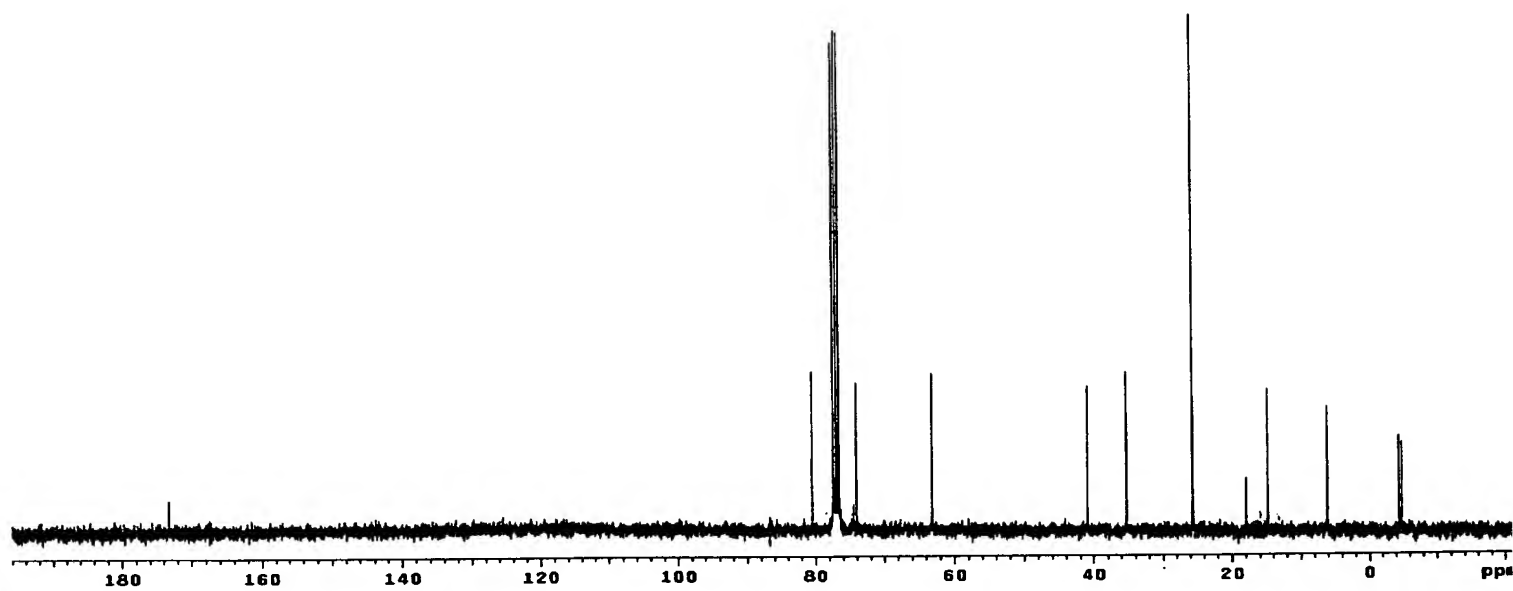
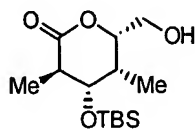
75MHz  $^{13}\text{C}$  NMR of compound **38** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



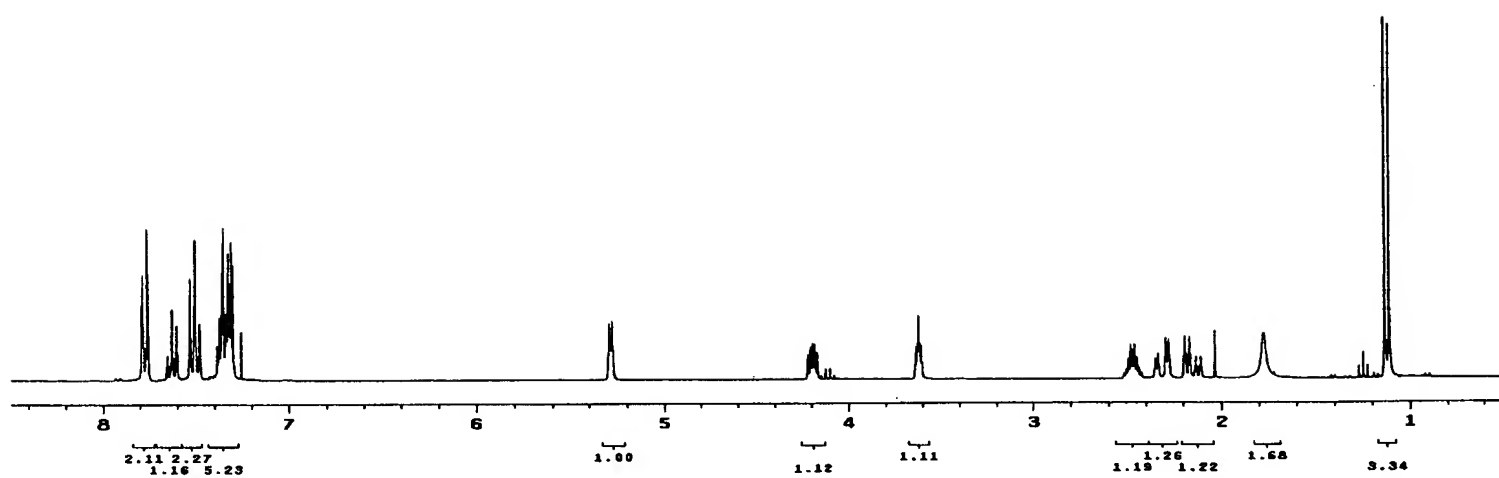
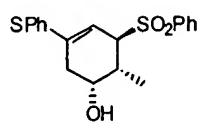
300MHz  $^1\text{H}$  NMR of compound 39 in  $\text{CDCl}_3$

**FIGURE 8 (Cont'd)**



75MHz  $^{13}\text{C}$  NMR of compound **39** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



300MHz <sup>1</sup>H NMR of compound 43β in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)

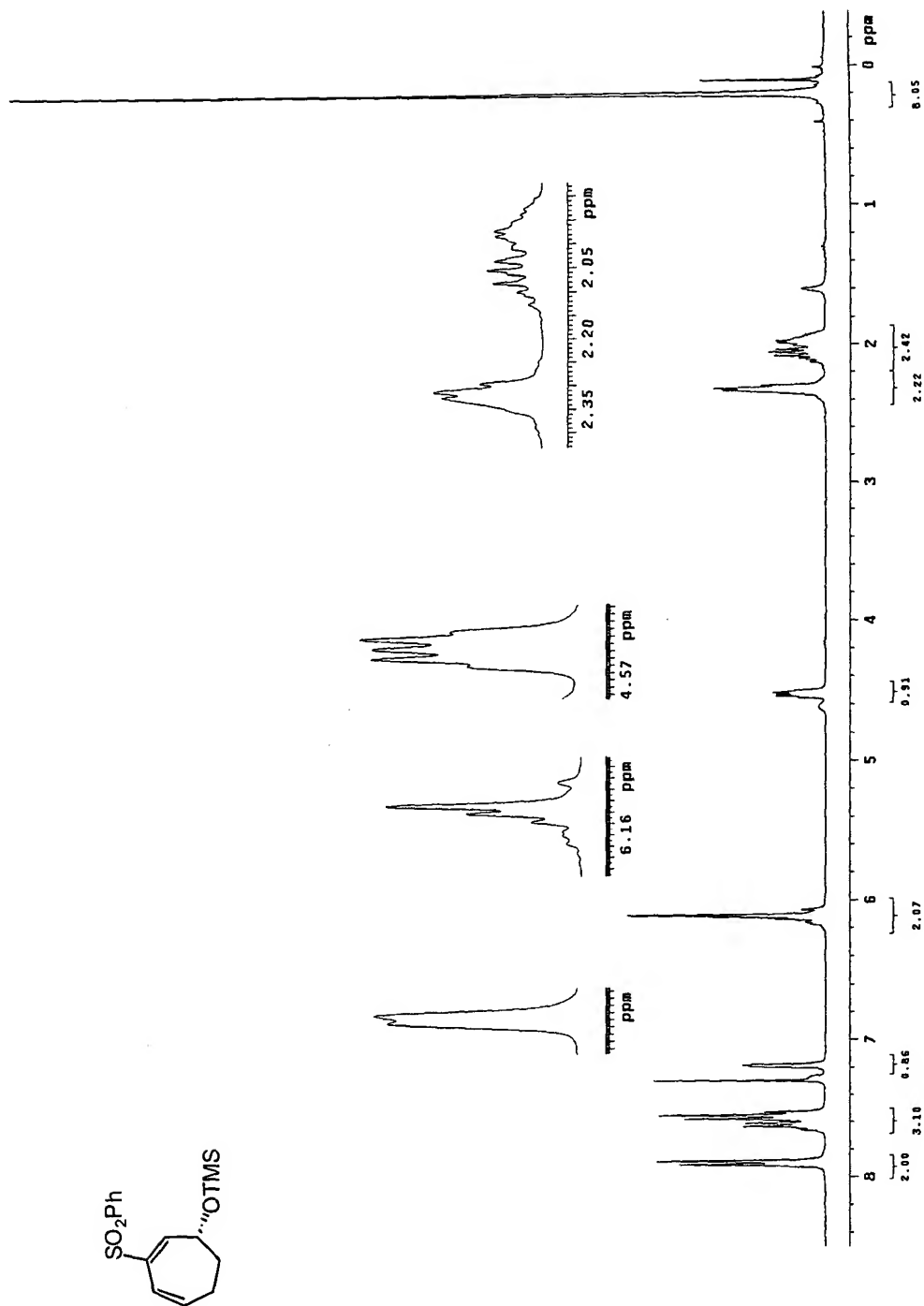
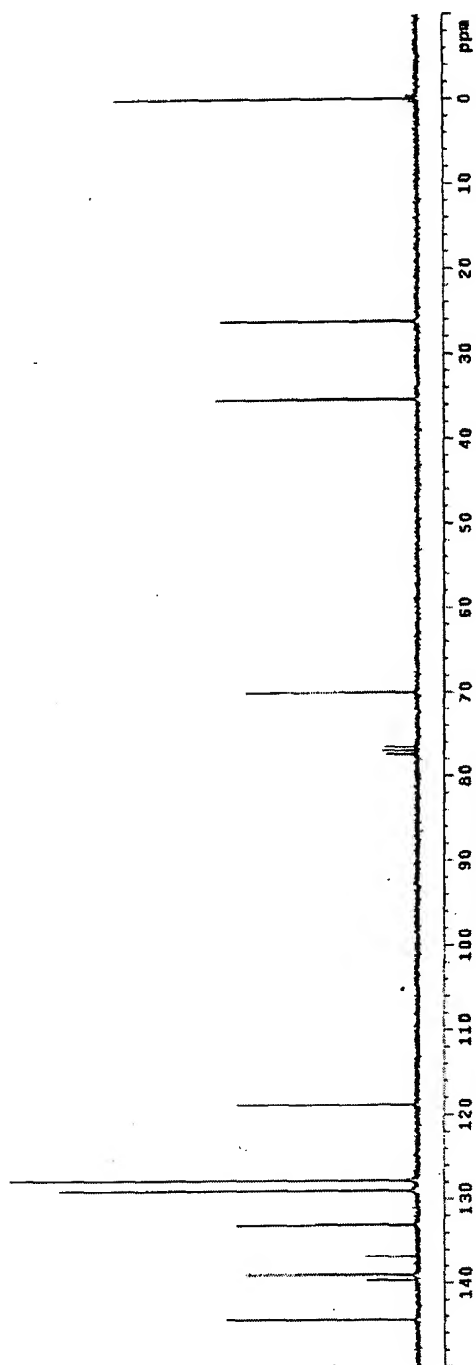
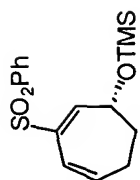
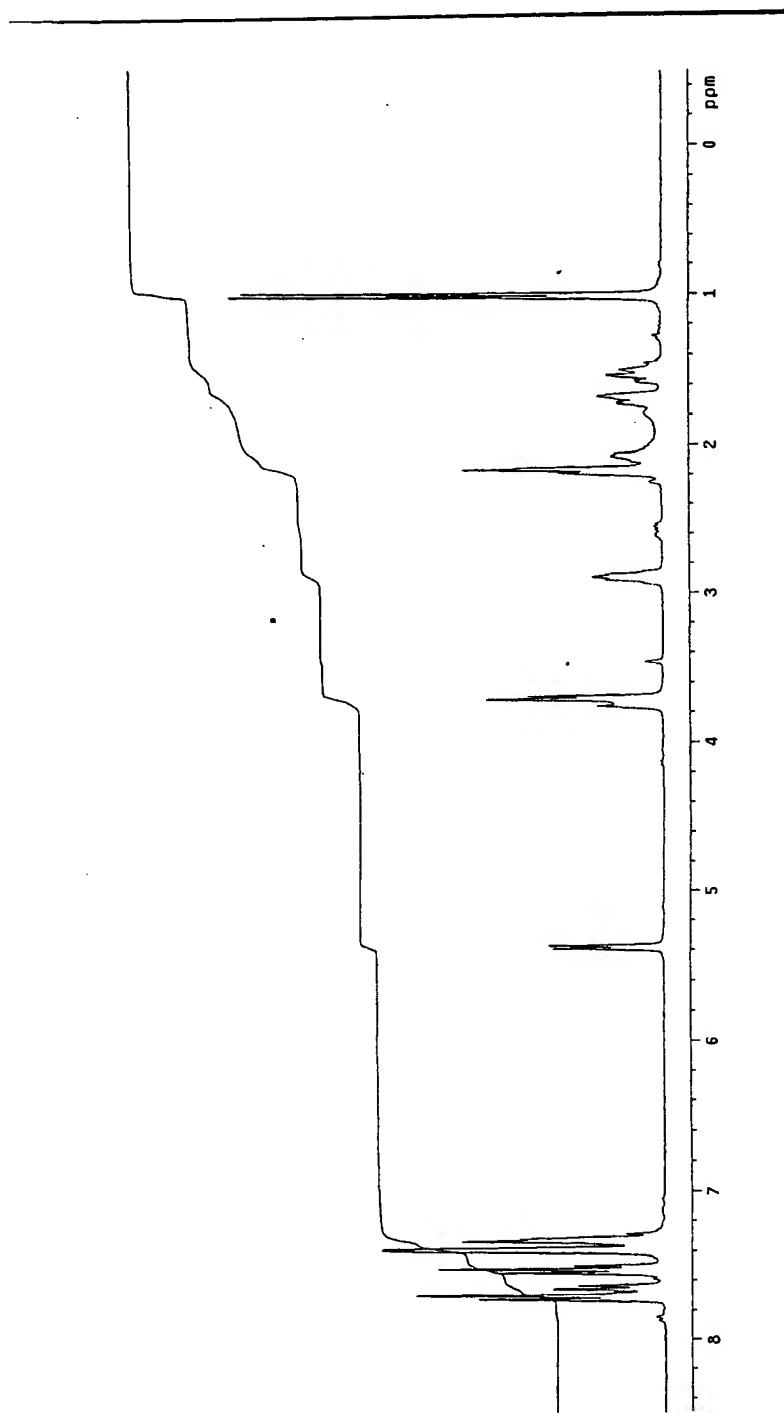
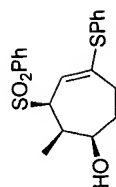


FIGURE 8 (Cont'd)



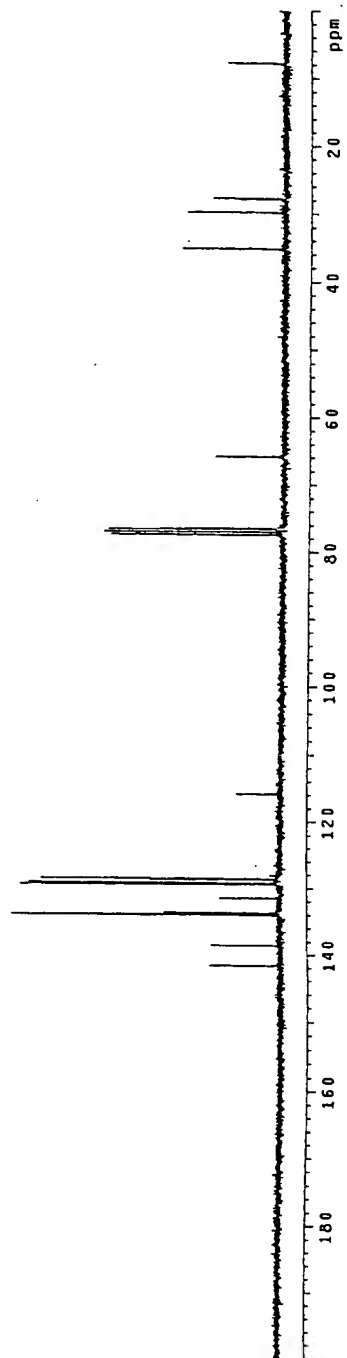
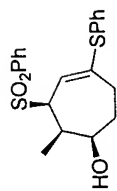
75MHz  $^{13}\text{C}$  NMR of compound 13 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



300MHz <sup>1</sup>H NMR of compound 21 in CDCl<sub>3</sub> 3

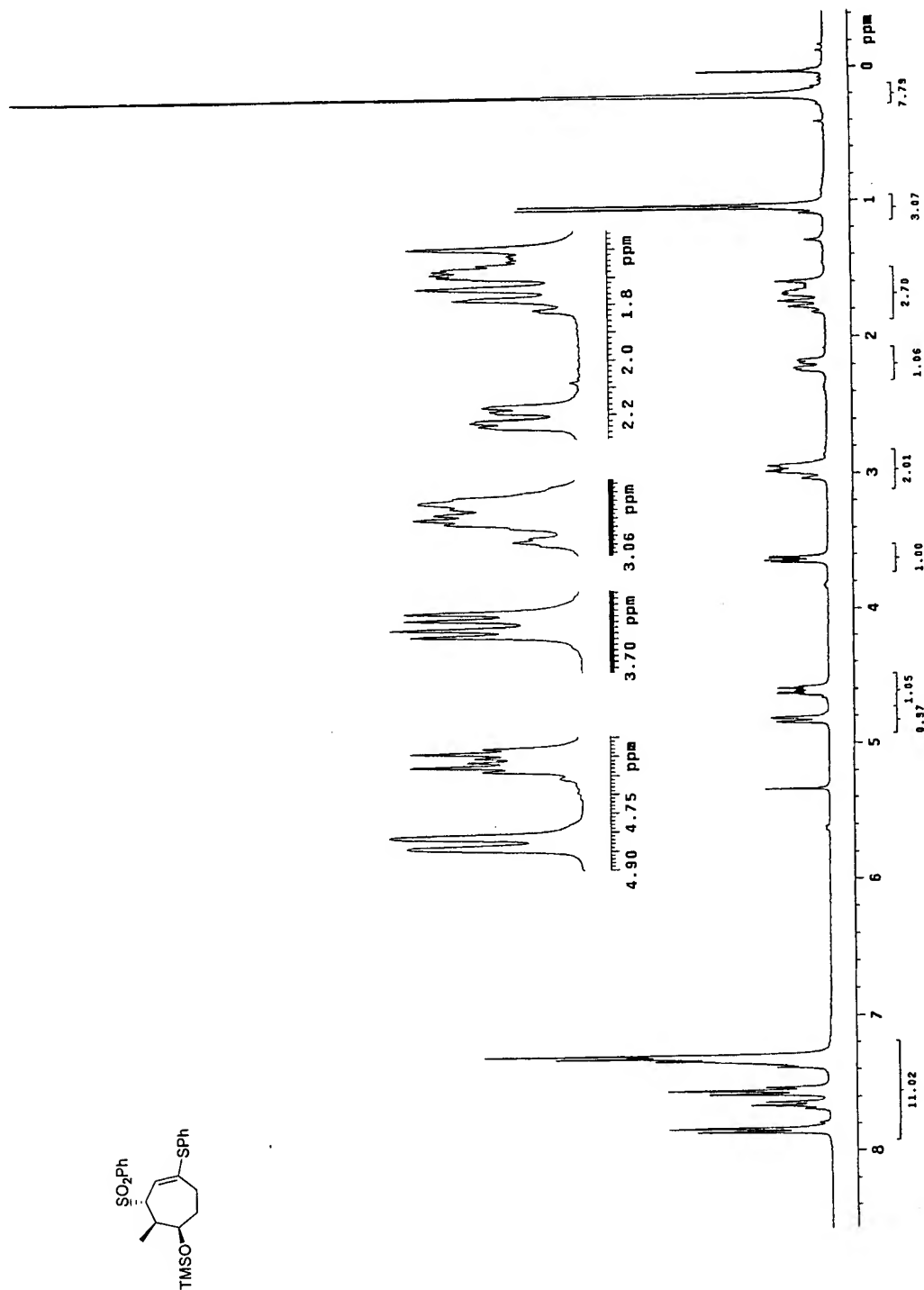
FIGURE 8 (Cont'd)



75MHz <sup>13</sup>C NMR of compound 21 in CDCl<sub>3</sub>

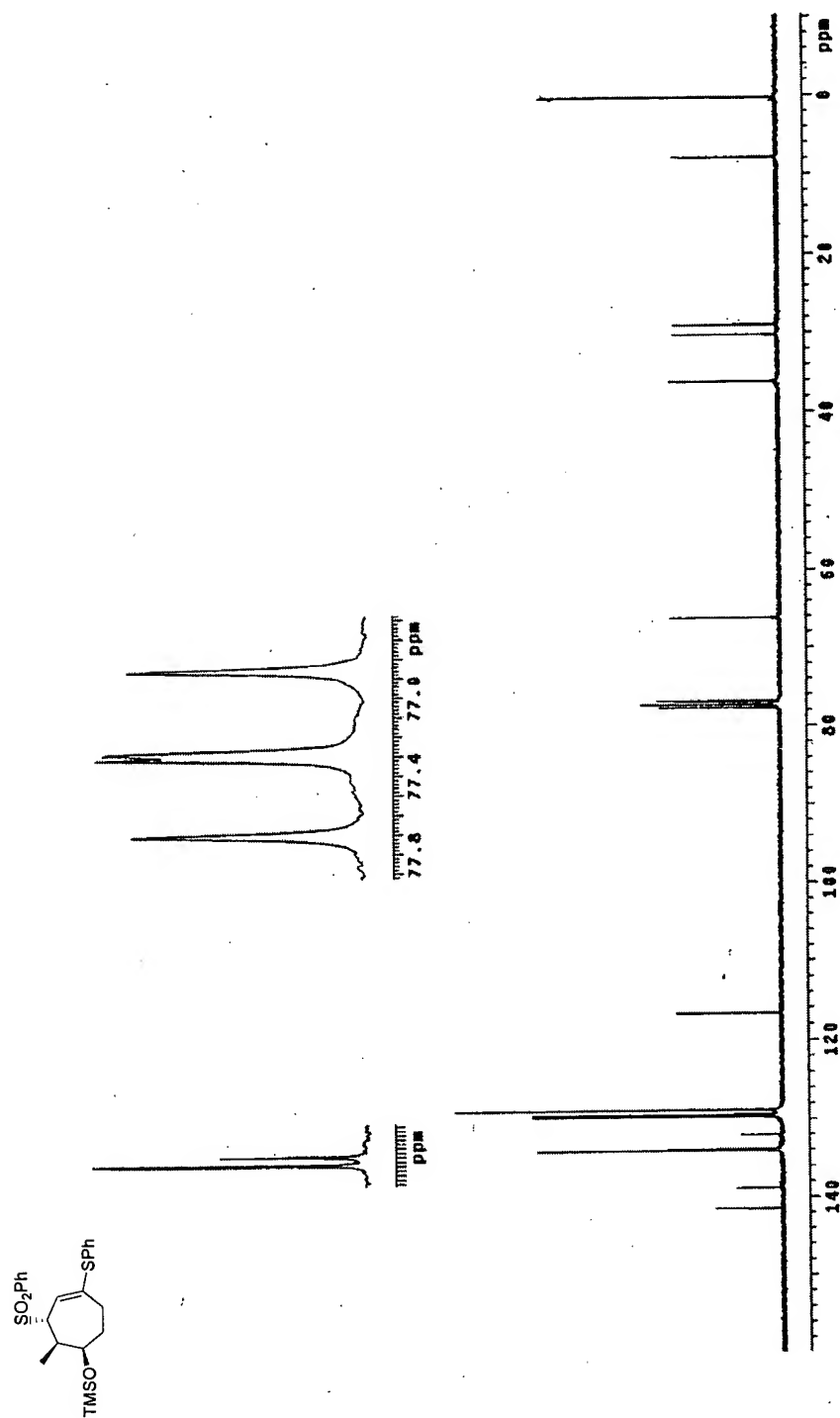


FIGURE 8 (Cont'd)



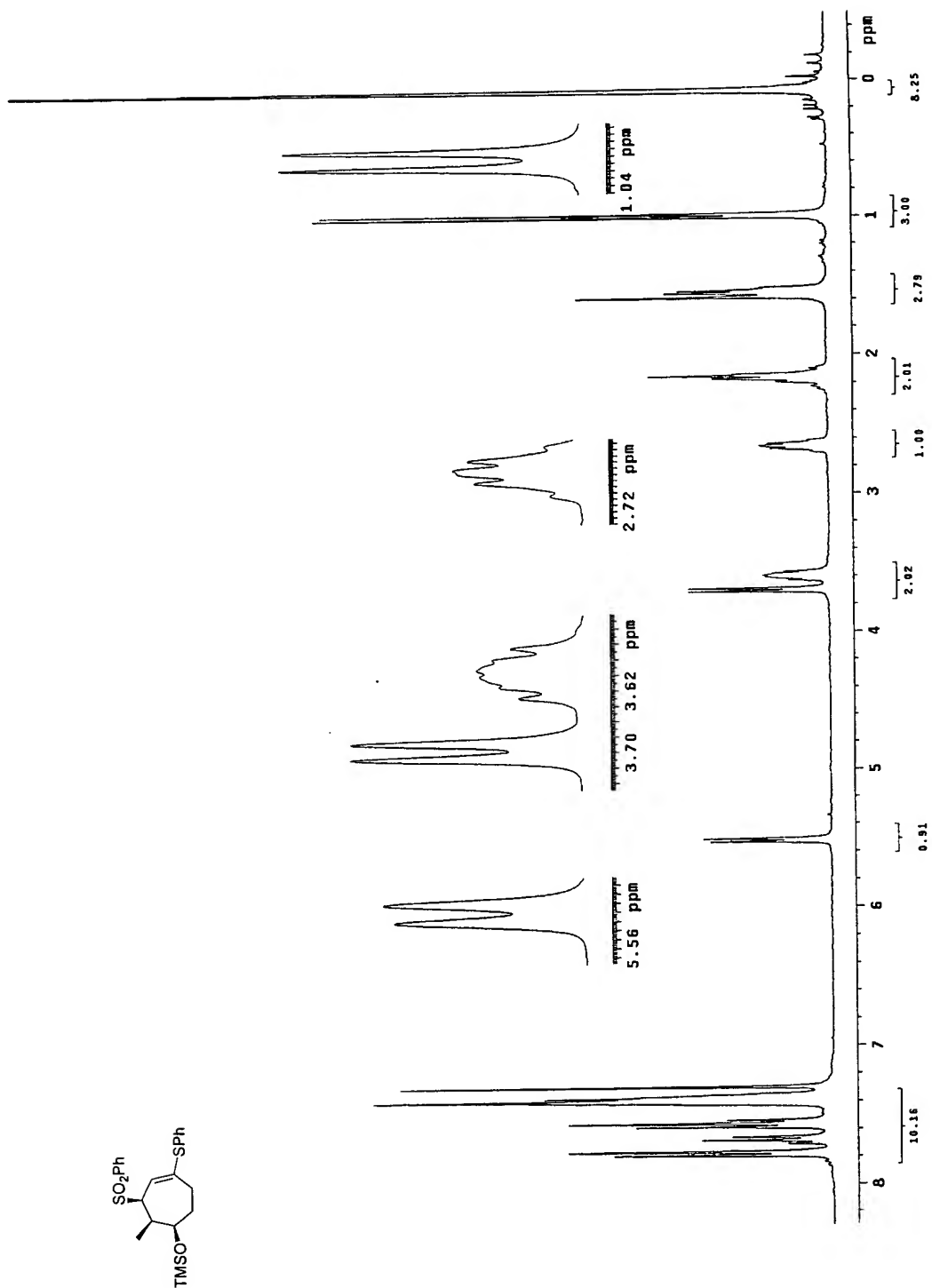
300MHz  $^1\text{H}$  NMR of compound 23  $\alpha$  in  $\text{CDCl}_3$  3

FIGURE 8 (Cont'd)



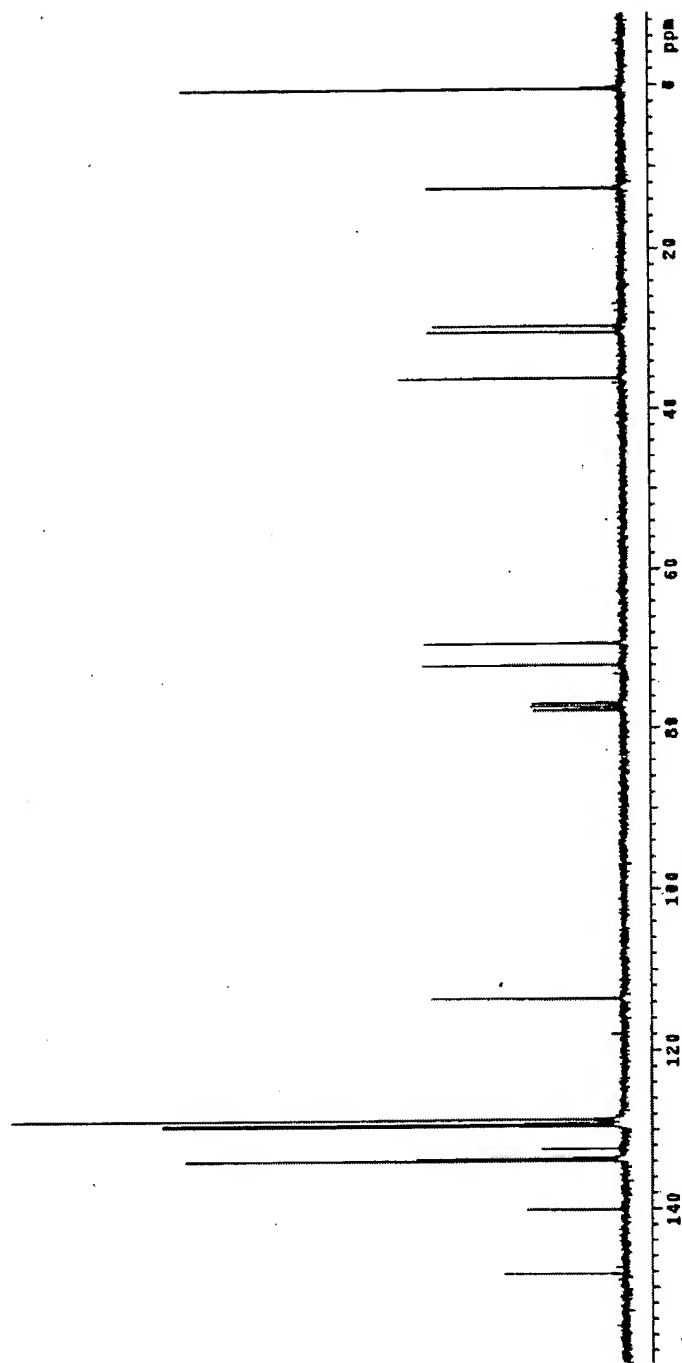
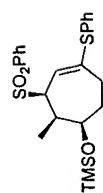
75MHz <sup>13</sup>C NMR of compound 23  $\alpha$  in CDCl<sub>3</sub> 3

FIGURE 8 (Cont'd)



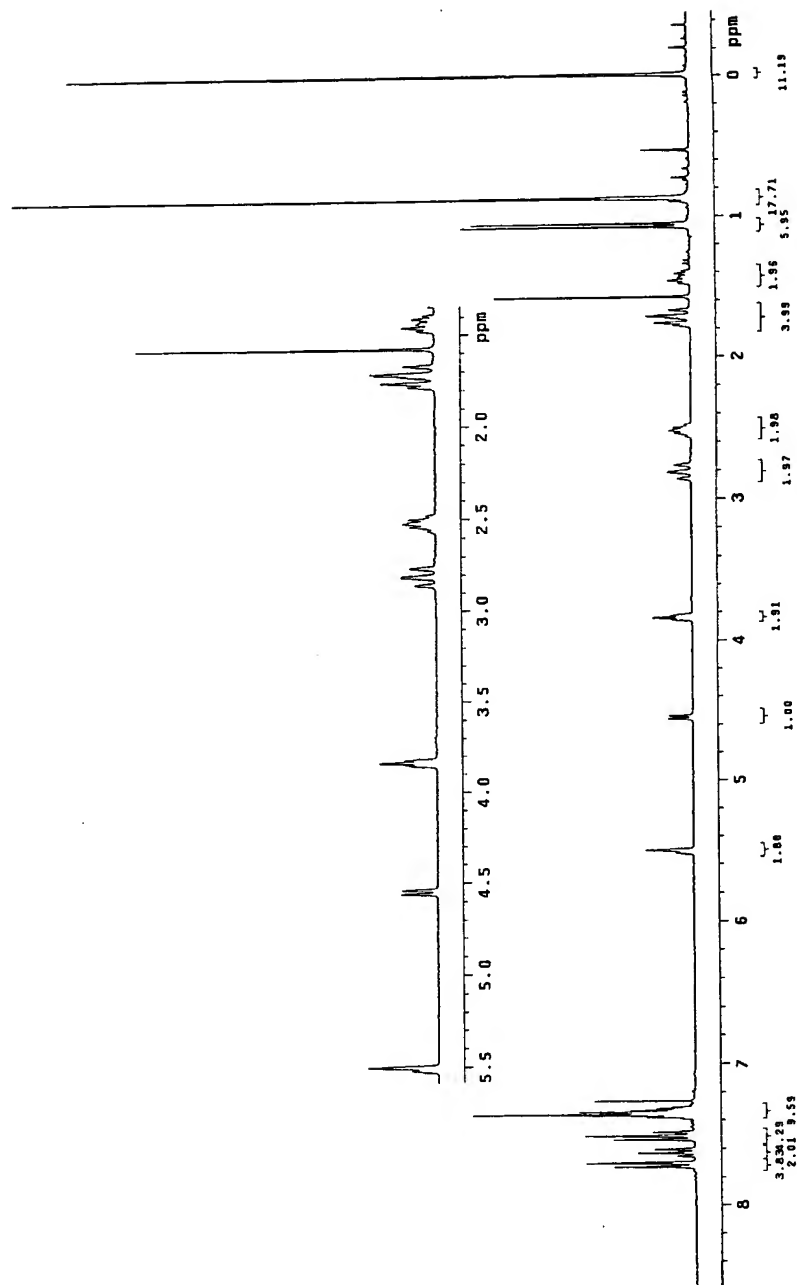
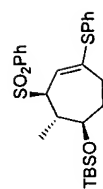
300MHz <sup>1</sup>H NMR of compound 23  $\beta$  in CDCl<sub>3</sub> 3

FIGURE 8 (Cont'd)



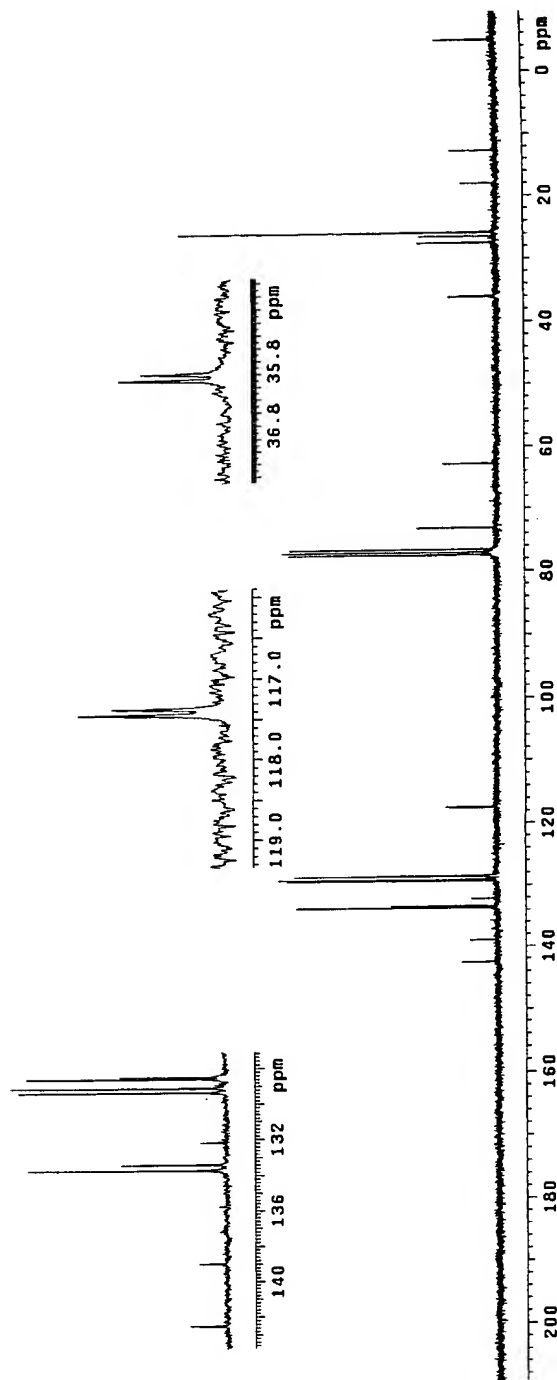
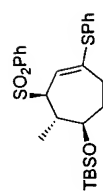
75MHz <sup>13</sup>C NMR of compound 23  $\beta$  in CDCl<sub>3</sub> 3

FIGURE 8 (Cont'd)



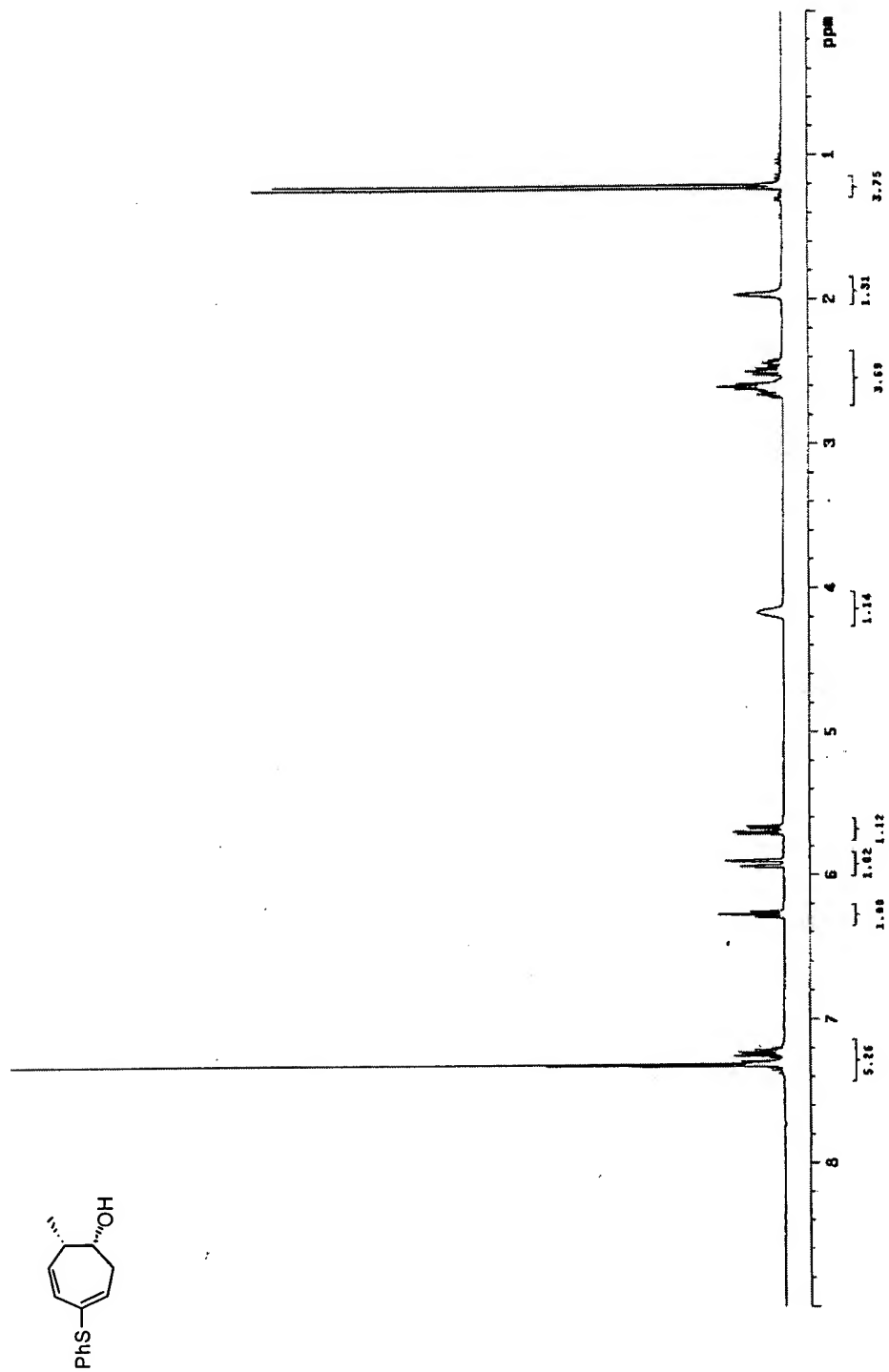
300MHz <sup>1</sup>H NMR of compound 22 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



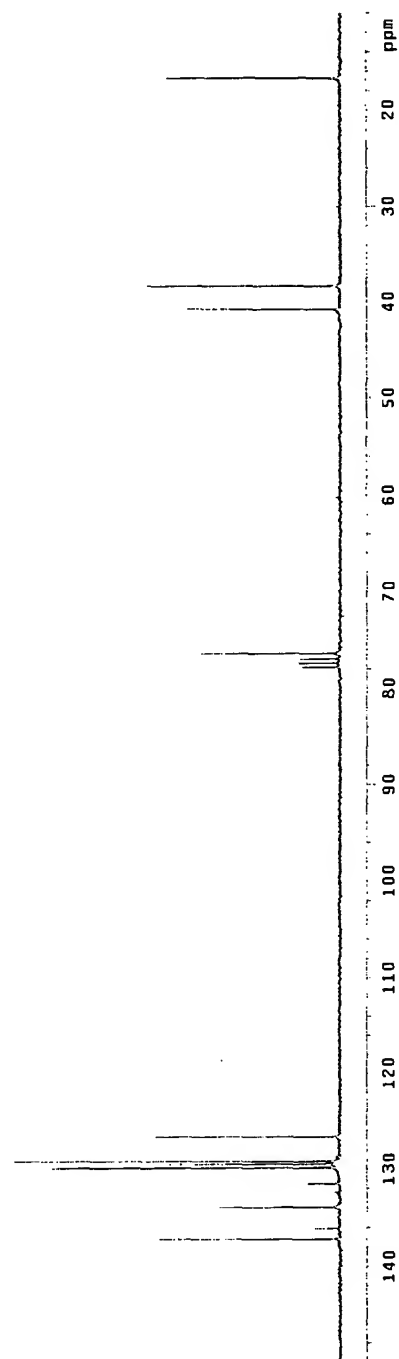
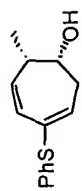
75MHz <sup>13</sup>C NMR of compound 22 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



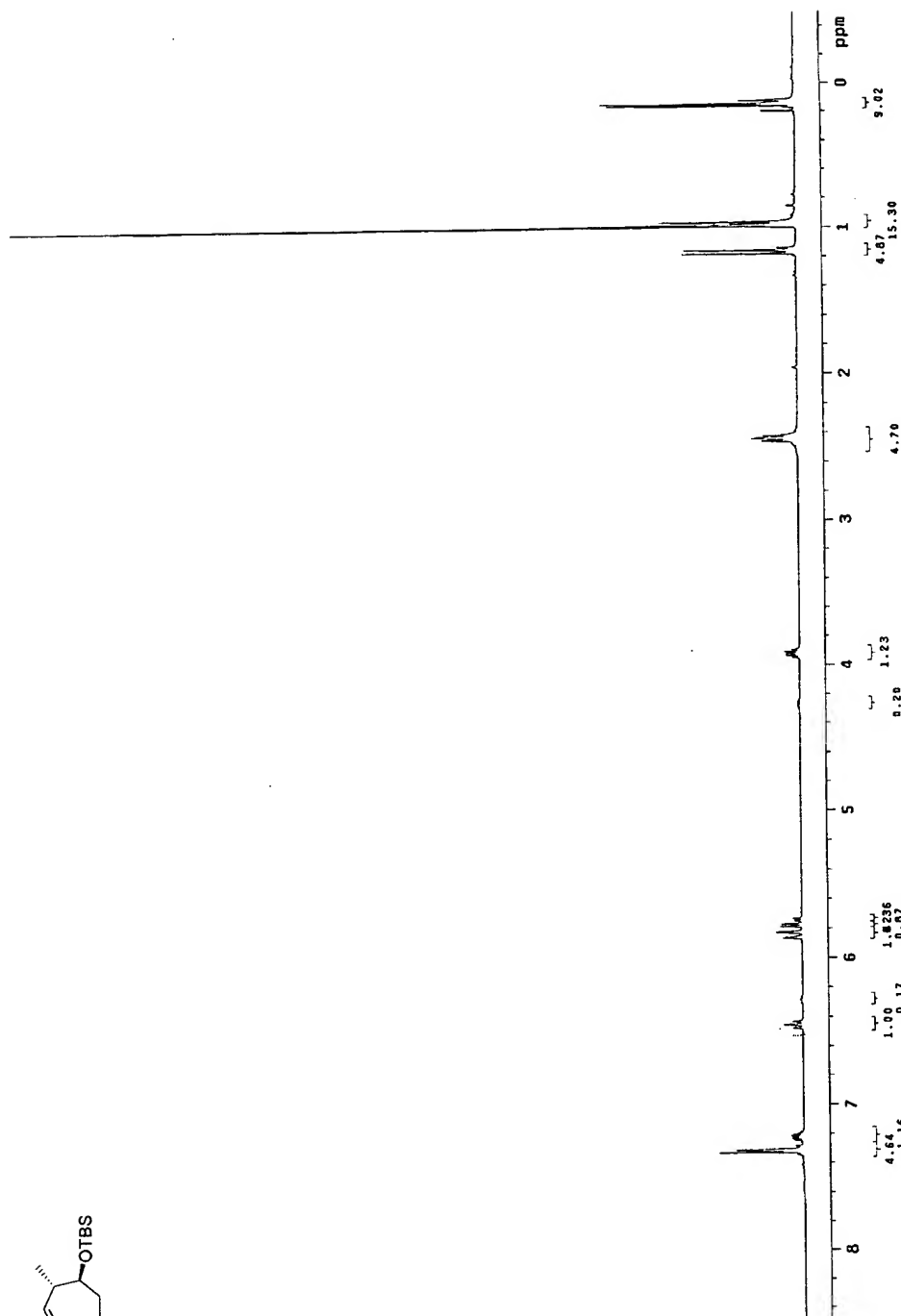
300MHz <sup>1</sup>H NMR of compound 29 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



75MHz <sup>13</sup>C NMR of compound 29 in CDCl<sub>3</sub>





300MHz  $^1\text{H}$  NMR of compound 27 in  $\text{CDCl}_3$

75MHz  $^{13}\text{C}$  NMR of compound 27 in  $\text{CDCl}_3$

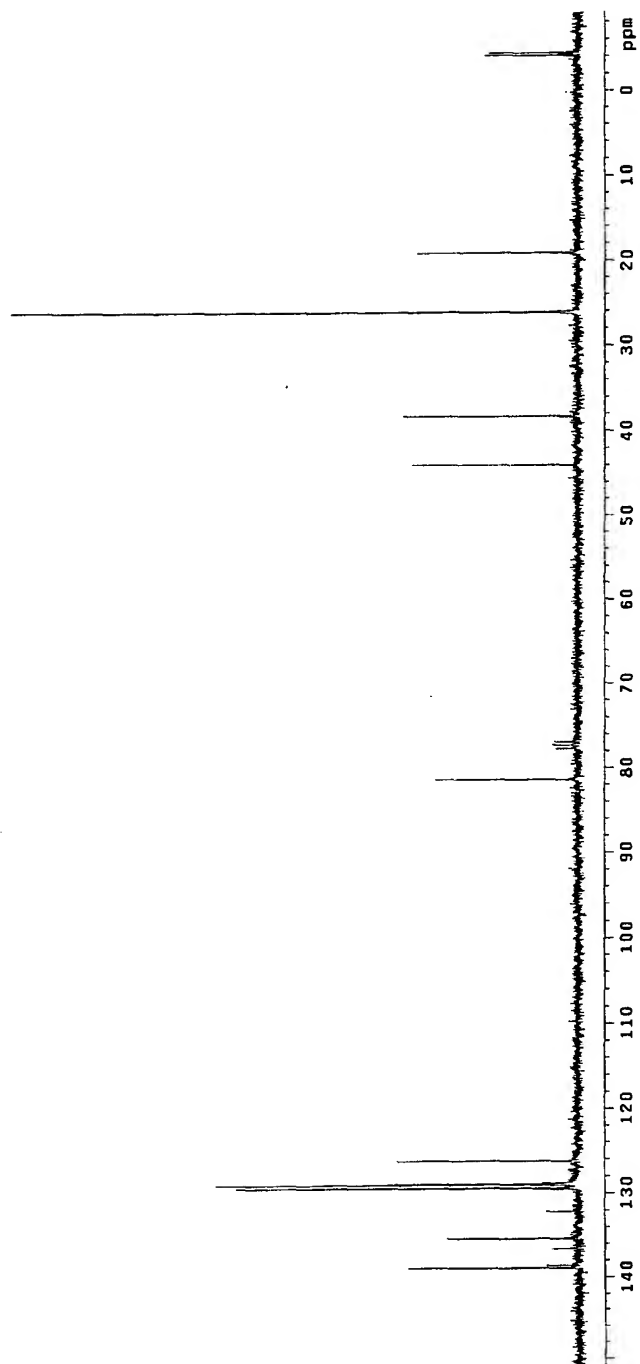
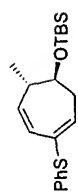


FIGURE 8 (Cont'd)

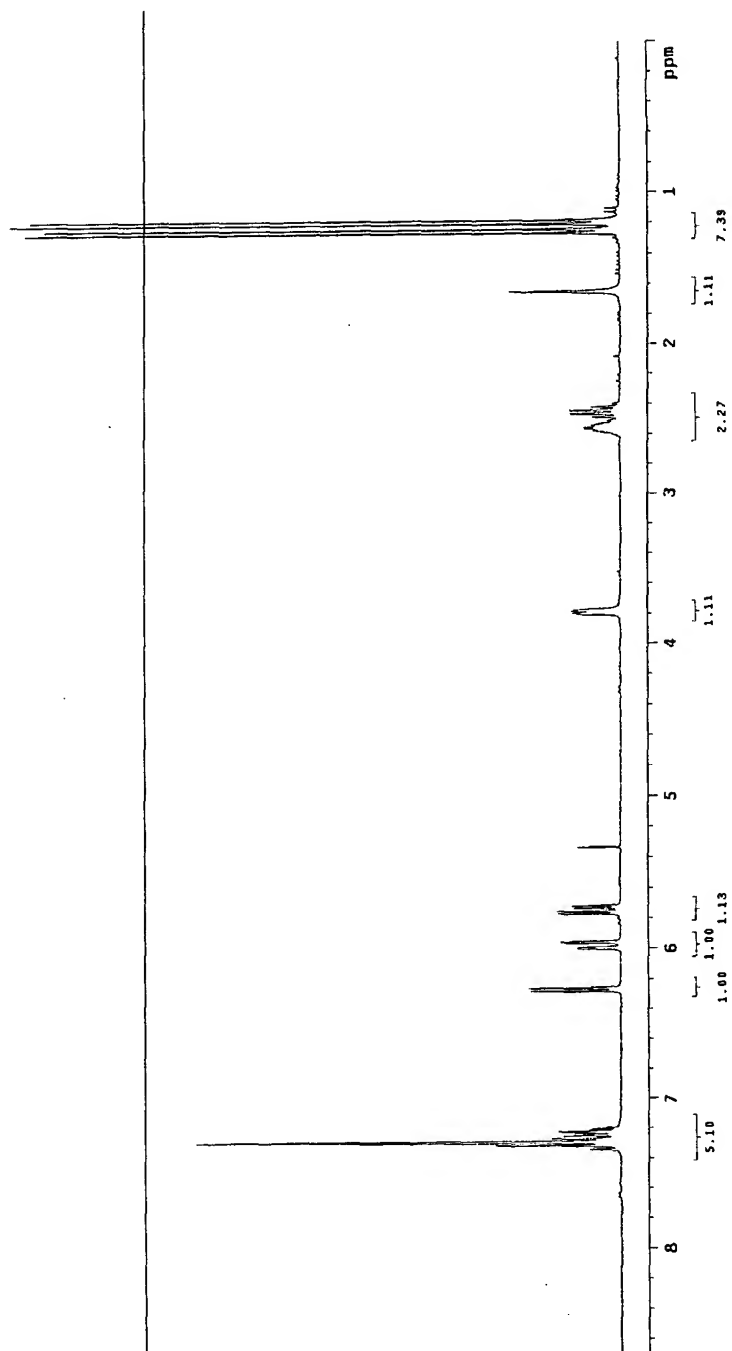
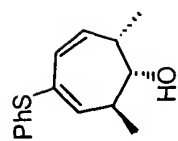
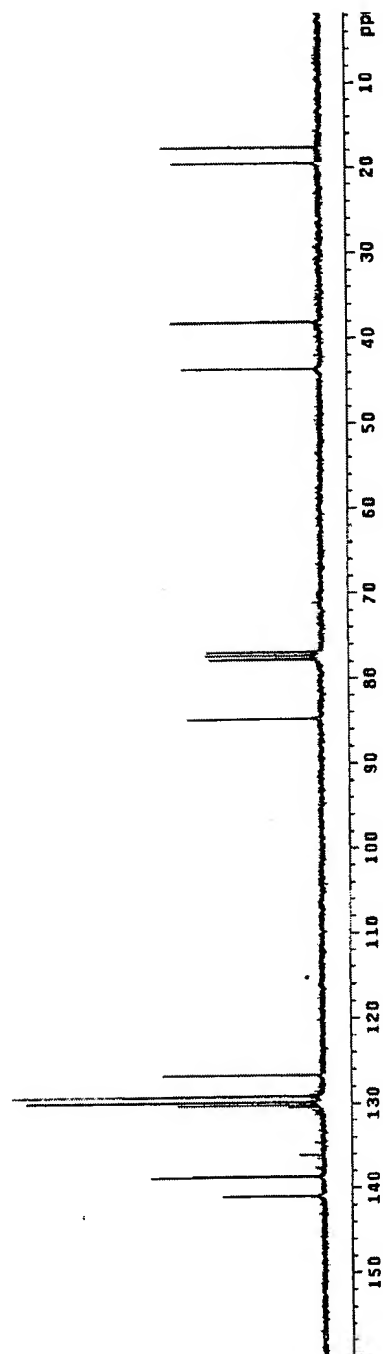
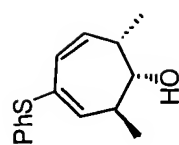
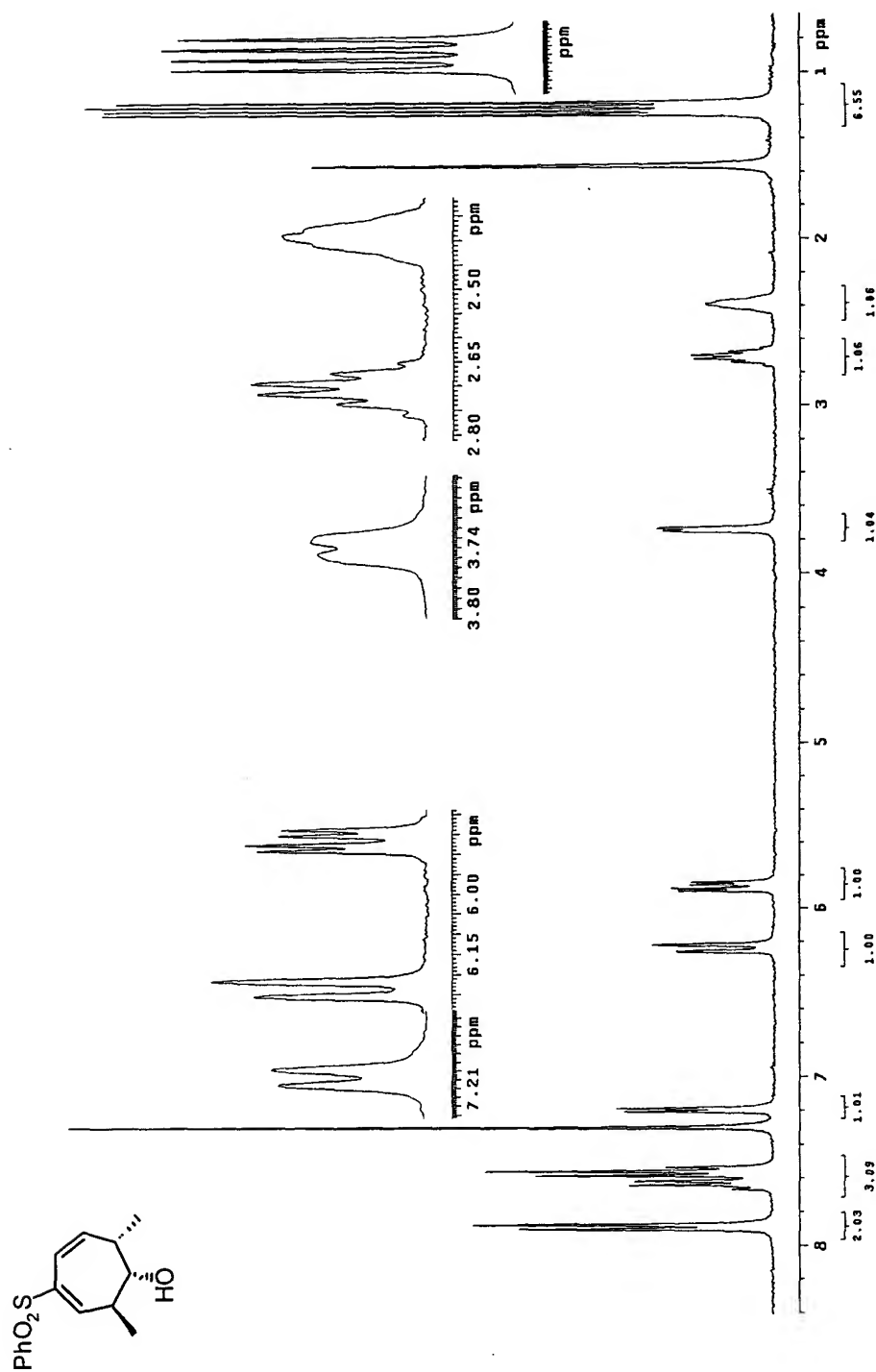


FIGURE 8 (Cont'd)



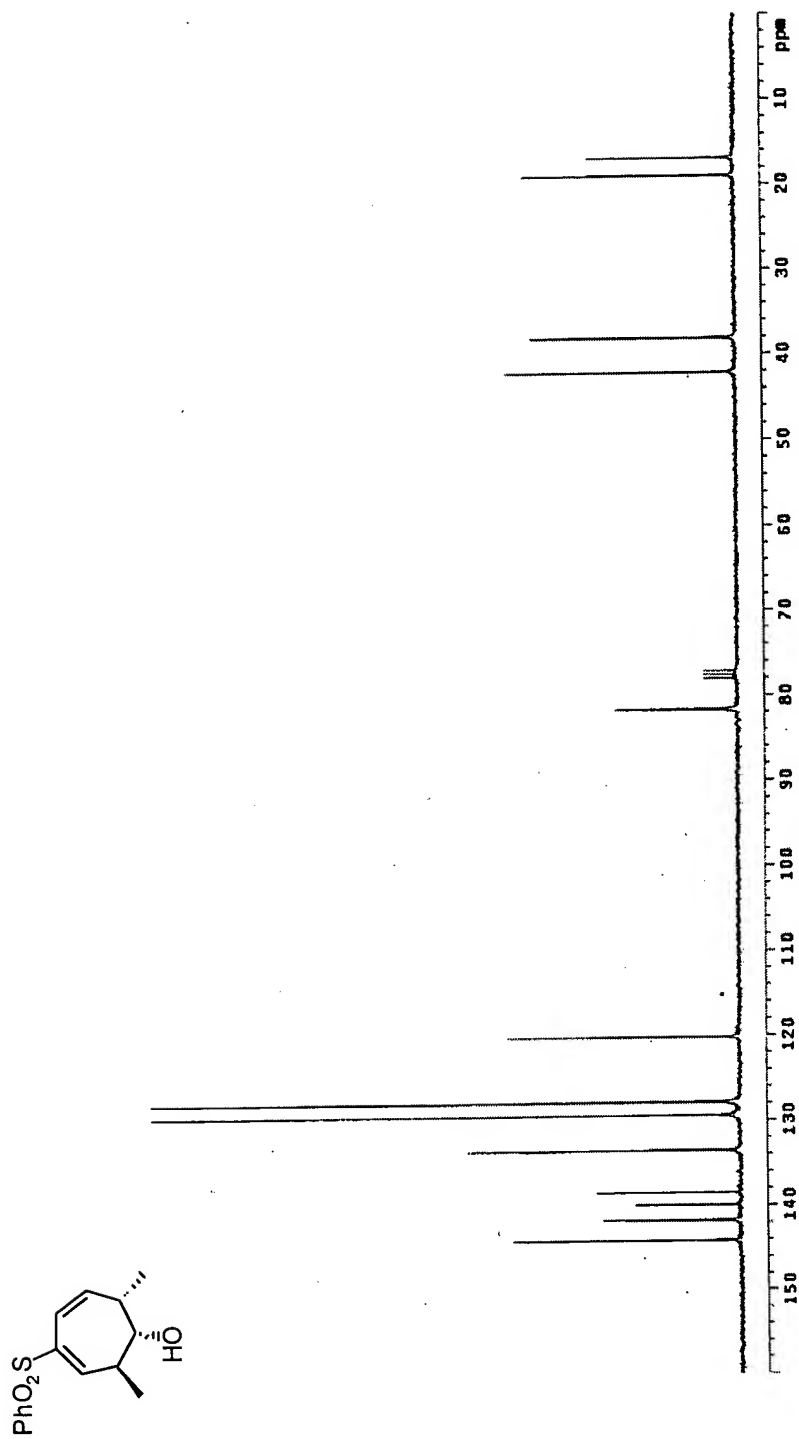
75MHz <sup>13</sup>C NMR of compound 31 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



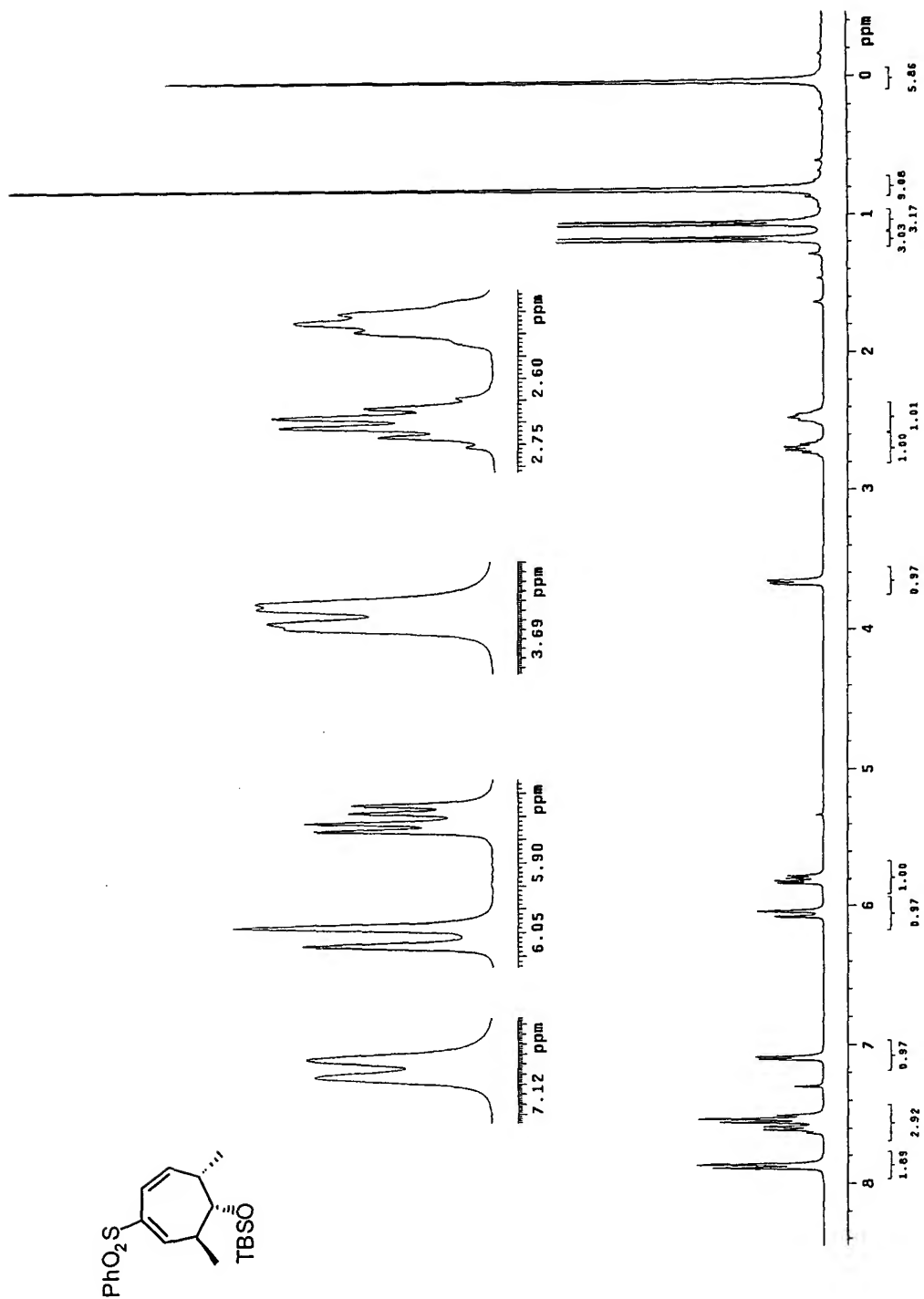
300MHz  $^1\text{H}$  NMR of compound 32 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)

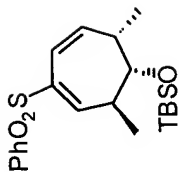


75MHz  $^{13}\text{C}$  NMR of compound 32 in  $\text{CDCl}_3$

300MHz  $^1\text{H}$  NMR of compound 33 in  $\text{CDCl}_3$



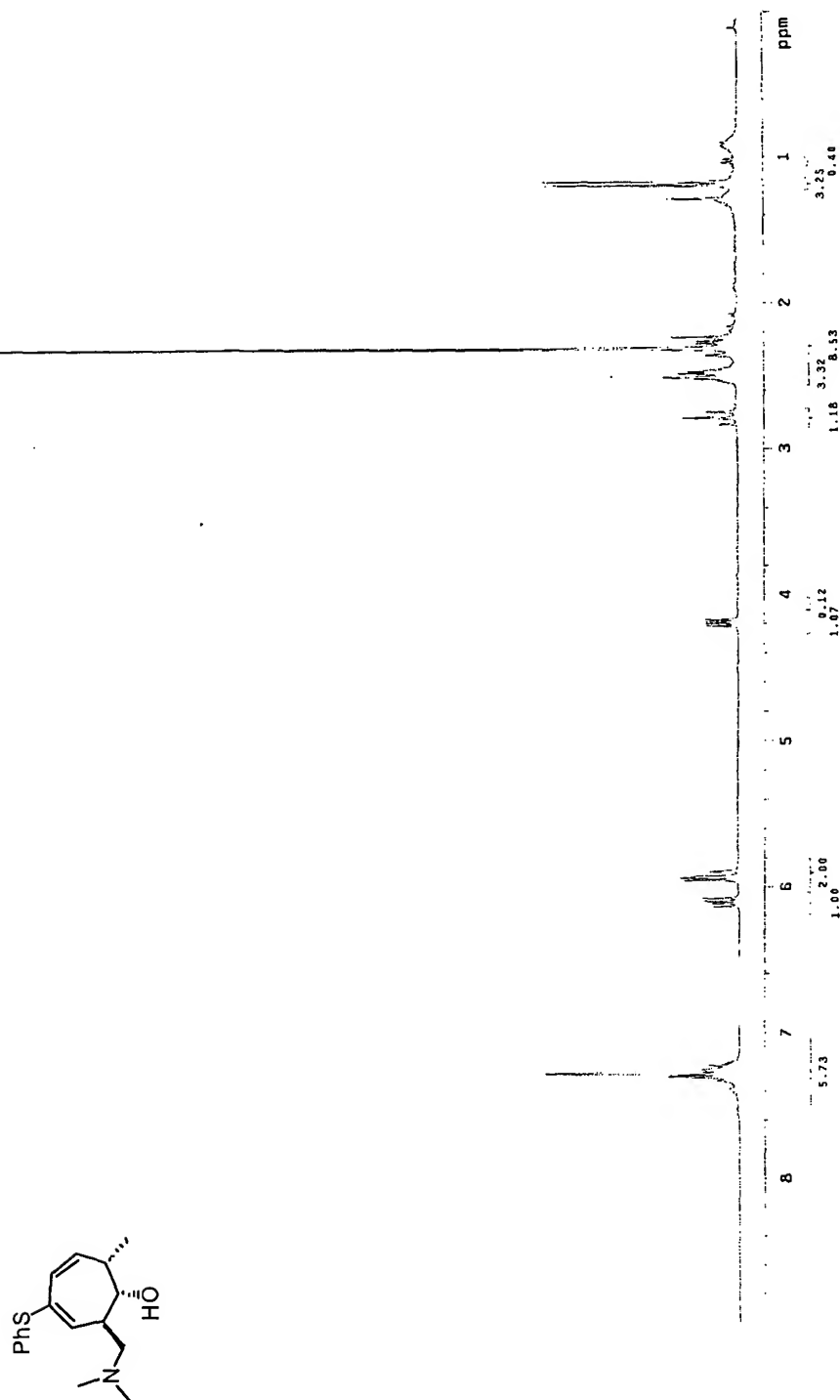
**FIGURE 8 (Cont'd)**



75MHz  $^{13}\text{C}$  NMR of compound 33 in  $\text{CDCl}_3$

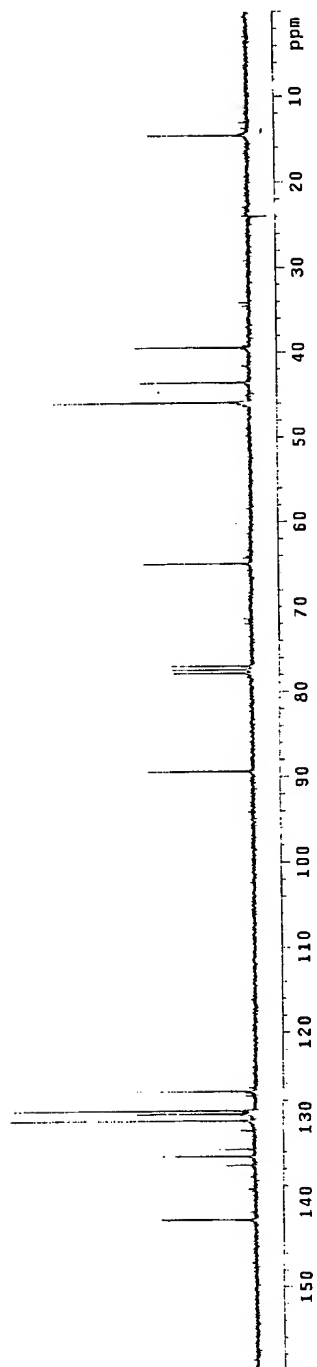
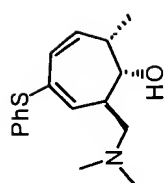


FIGURE 8 (Cont'd)



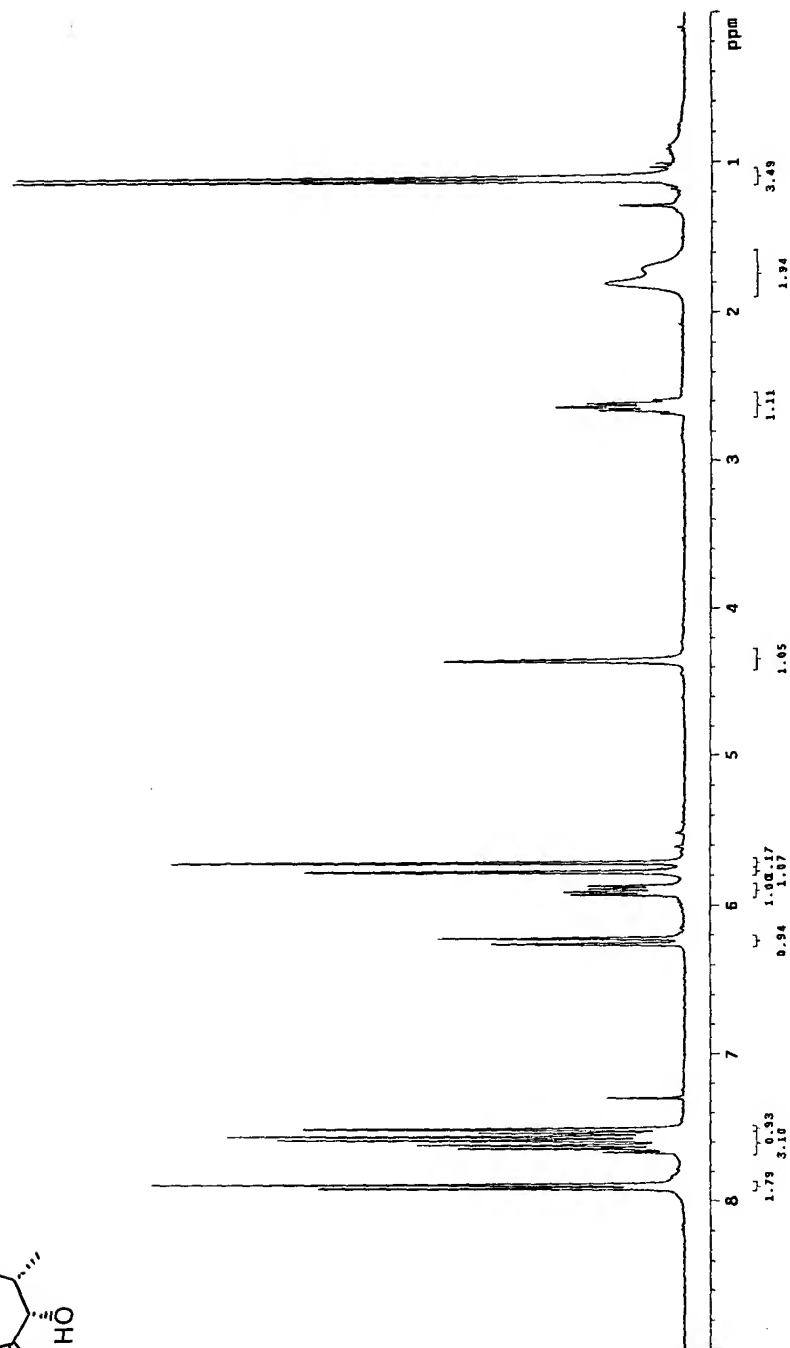
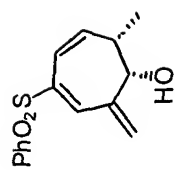
300MHz <sup>1</sup>H NMR of compound 34 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



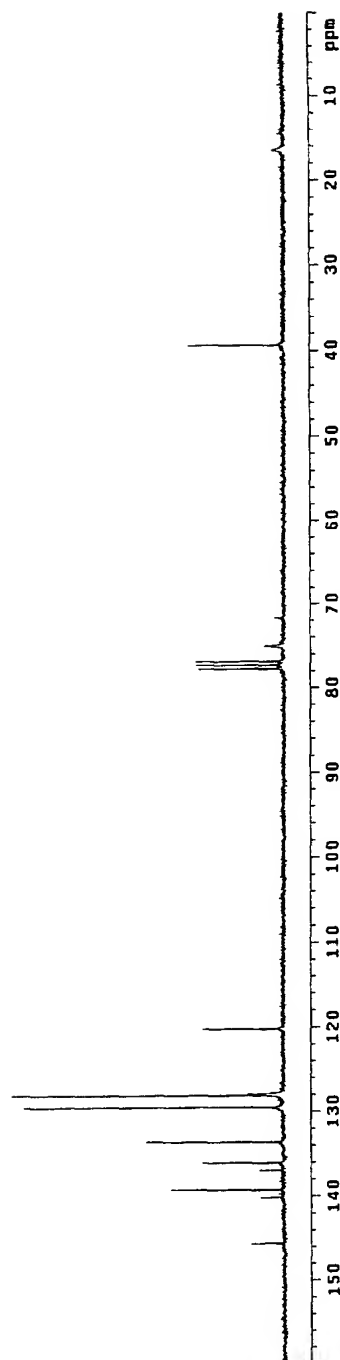
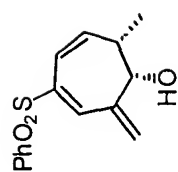
75MHz <sup>13</sup>C NMR of compound 34 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



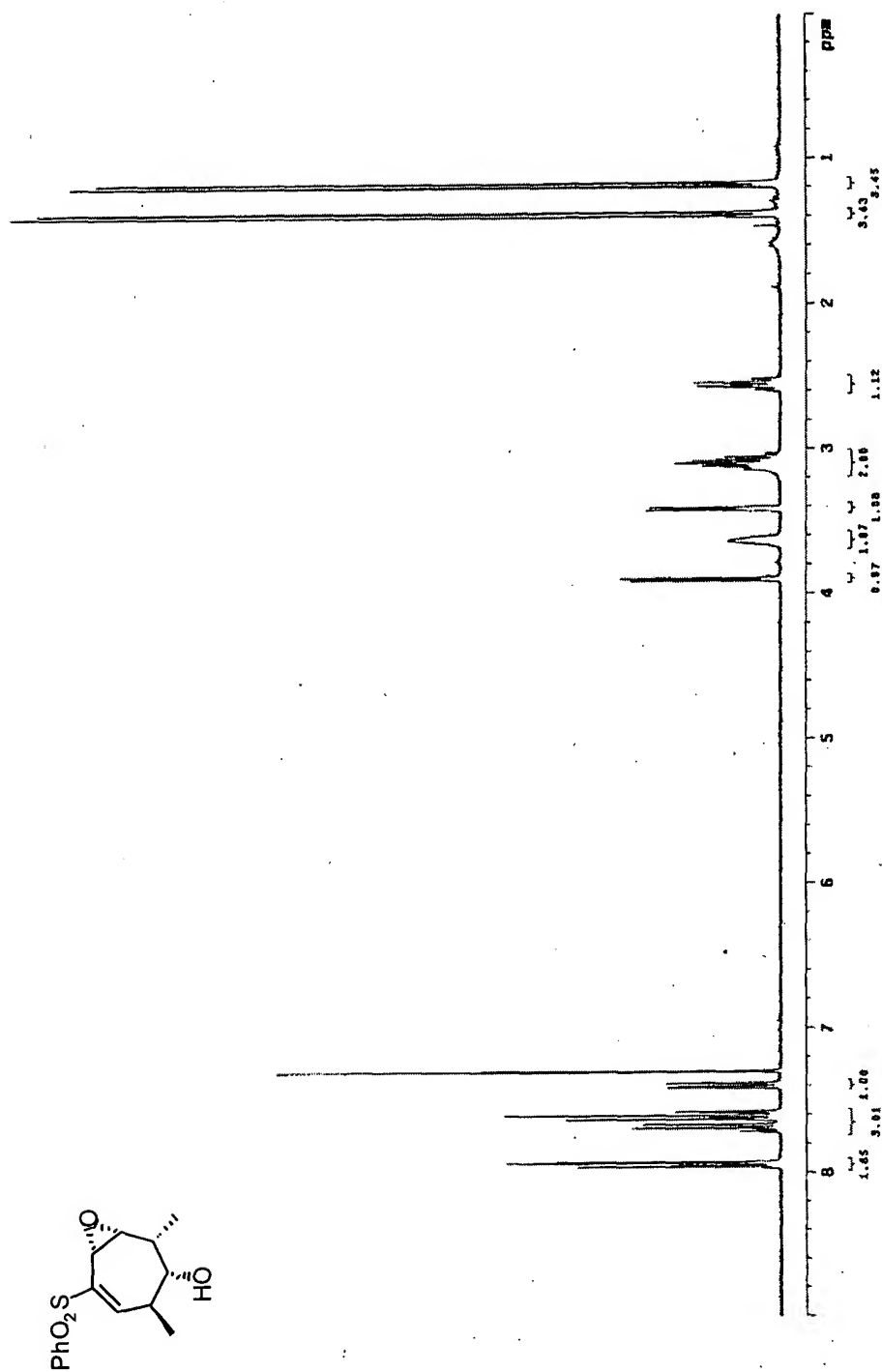
300MHz <sup>1</sup>H NMR of compound 35 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



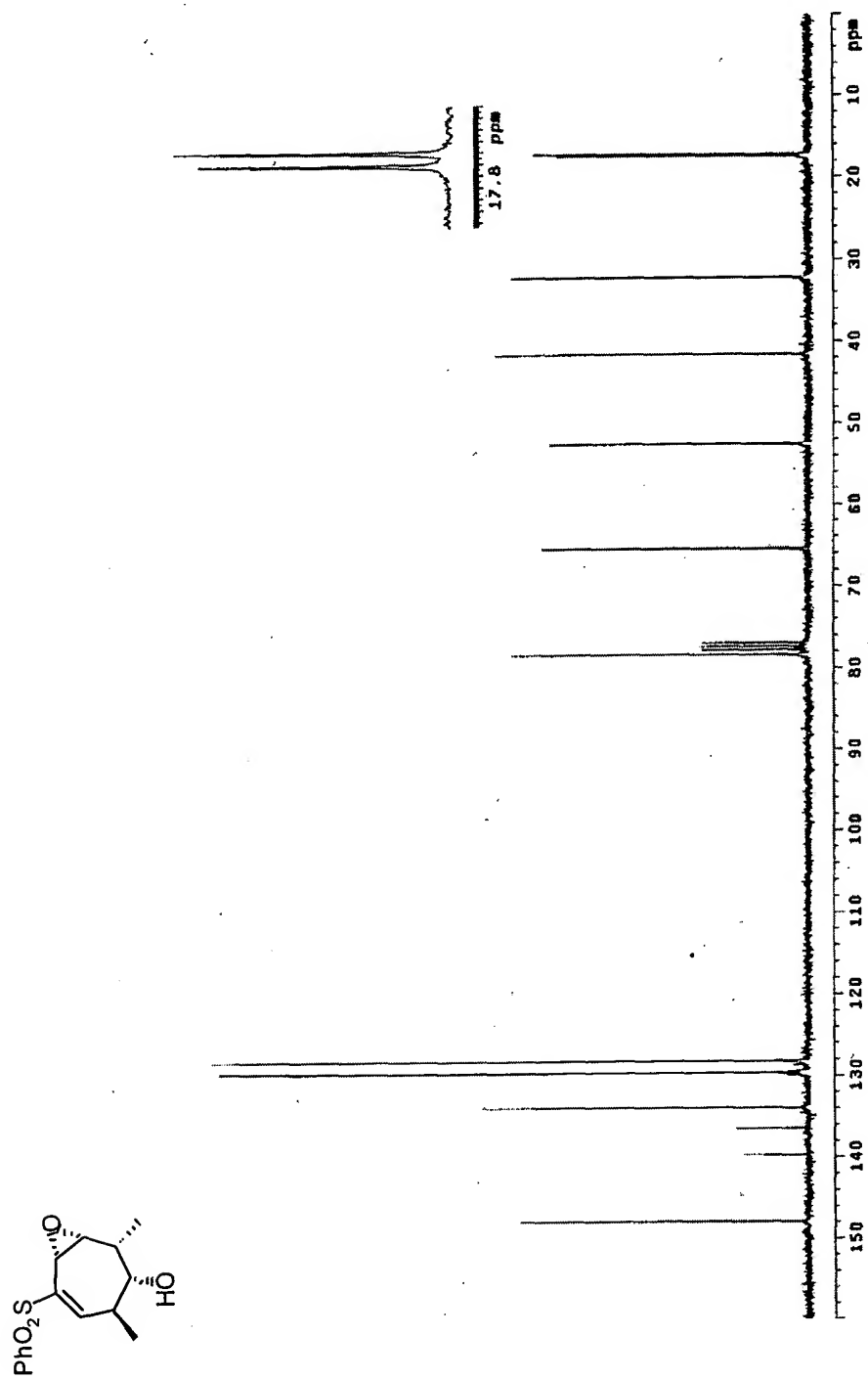
75MHz  $^{13}\text{C}$  NMR of compound 35 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



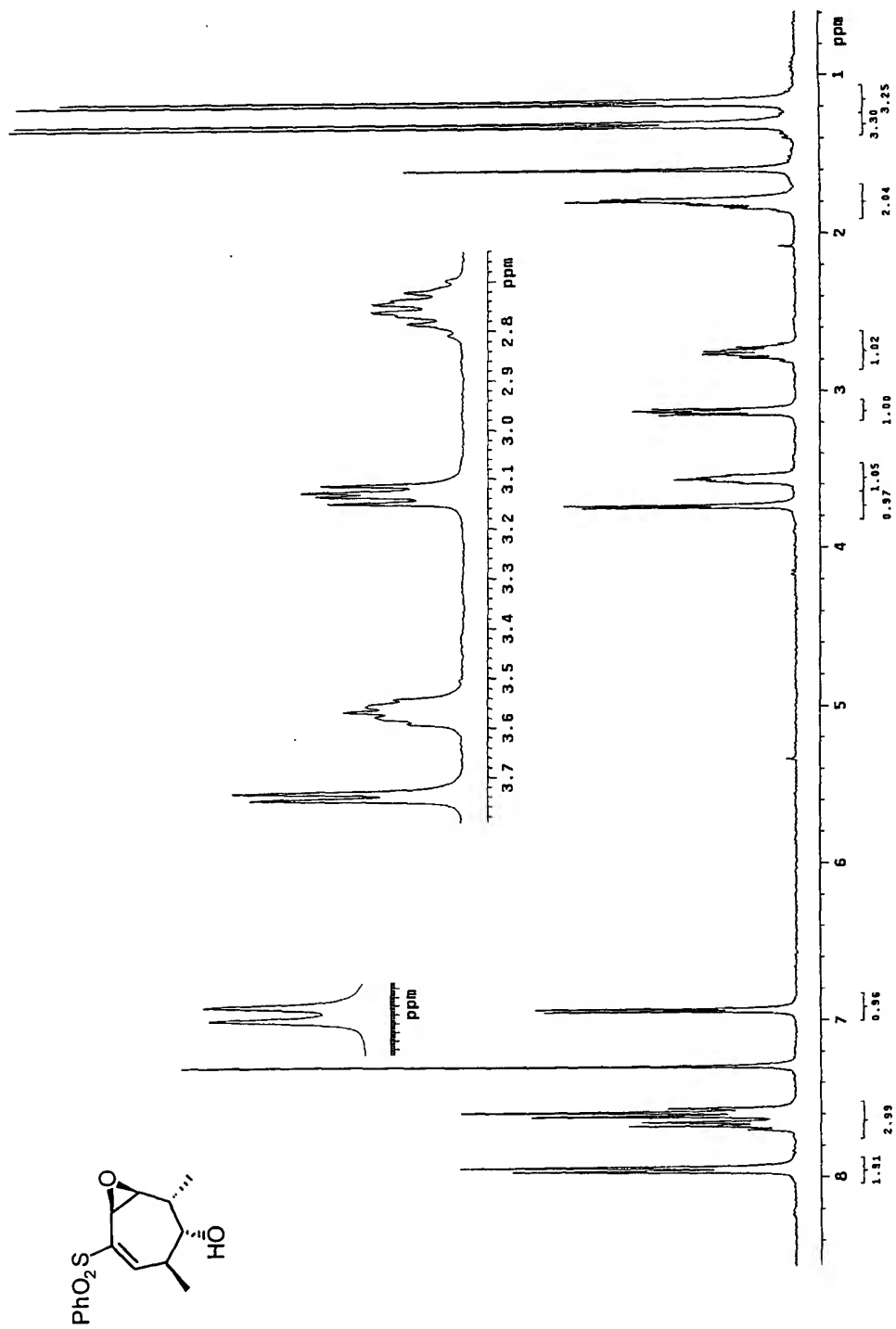
300MHz  $^1\text{H}$  NMR of compound  $\alpha 36$  in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



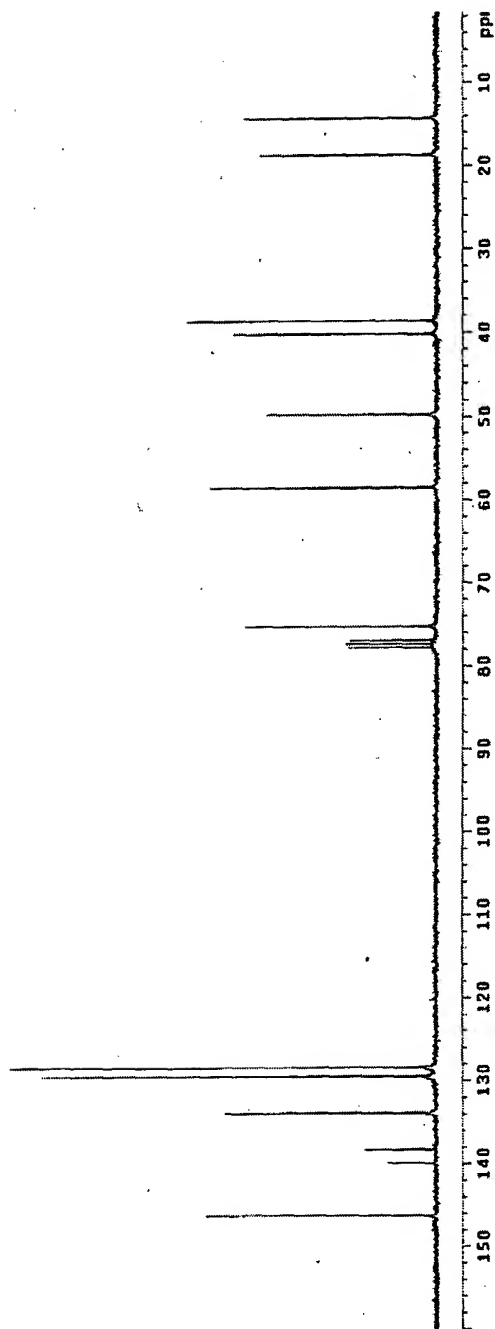
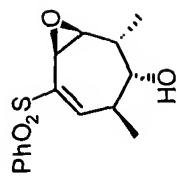
75MHz  $^{13}\text{C}$  NMR of compound  $\alpha 36$  in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



300MHz  $^1\text{H}$  NMR of compound **336** in  $\text{CDCl}_3$

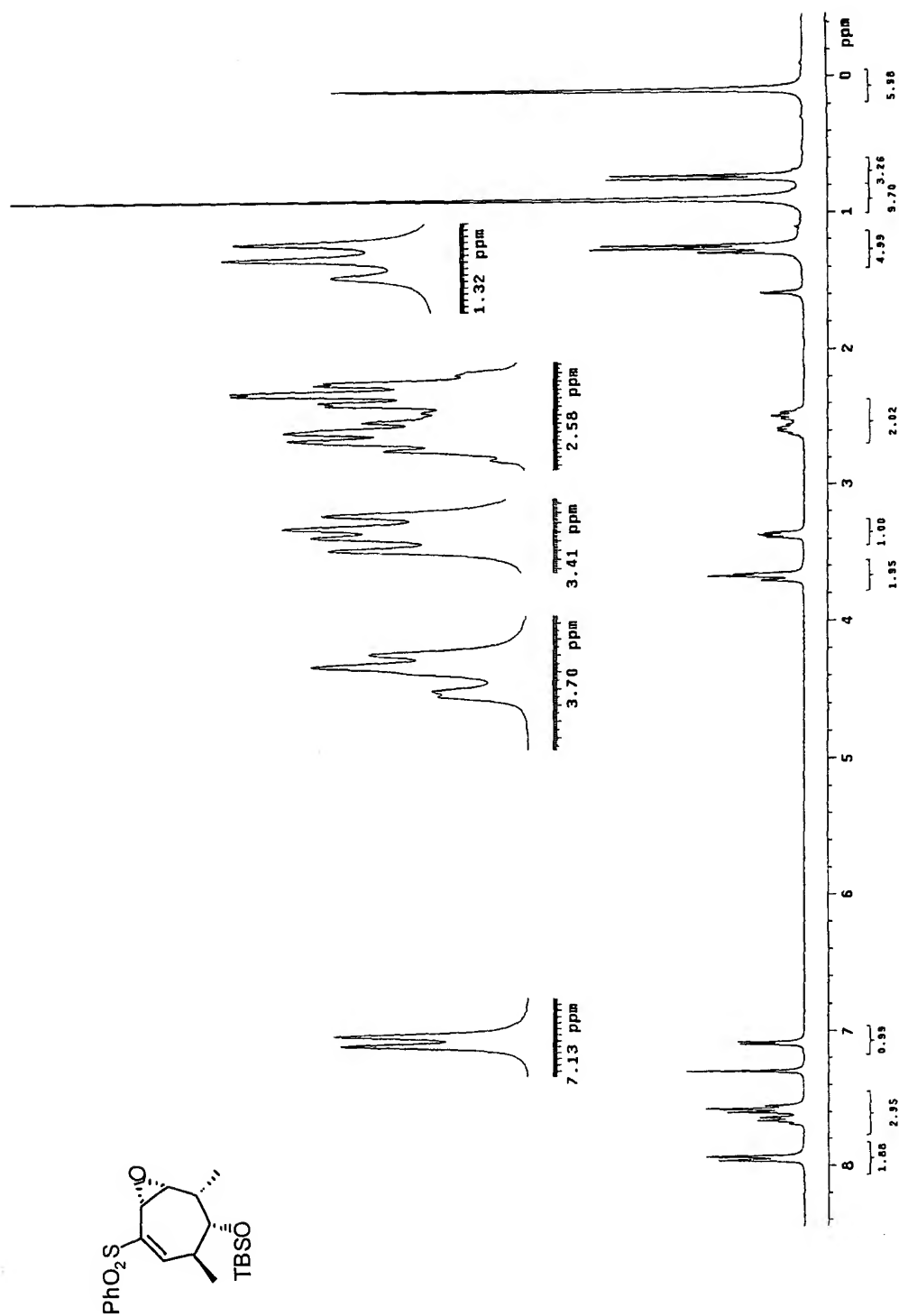
FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 36 in  $\text{CDCl}_3$

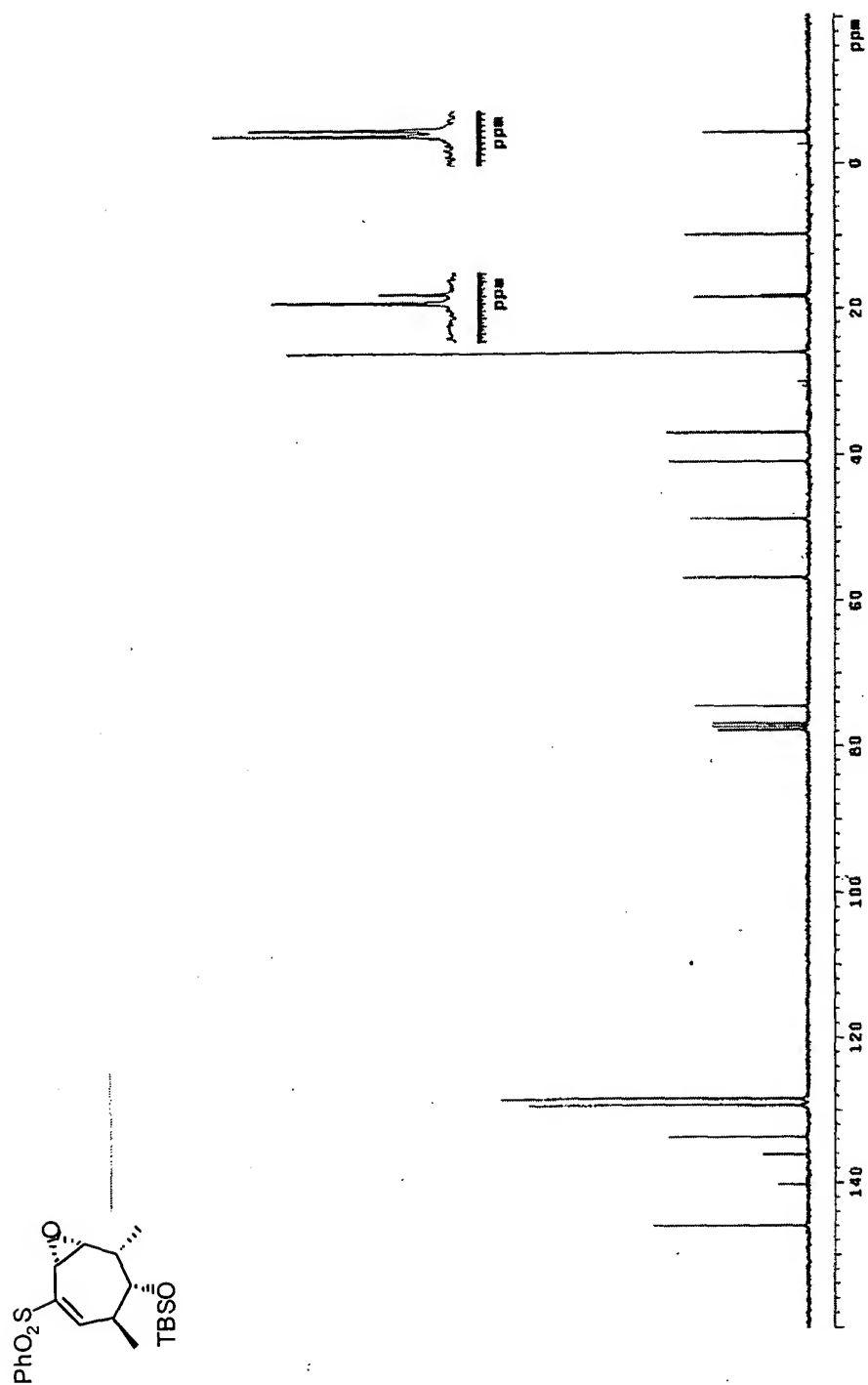


FIGURE 8 (Cont'd)



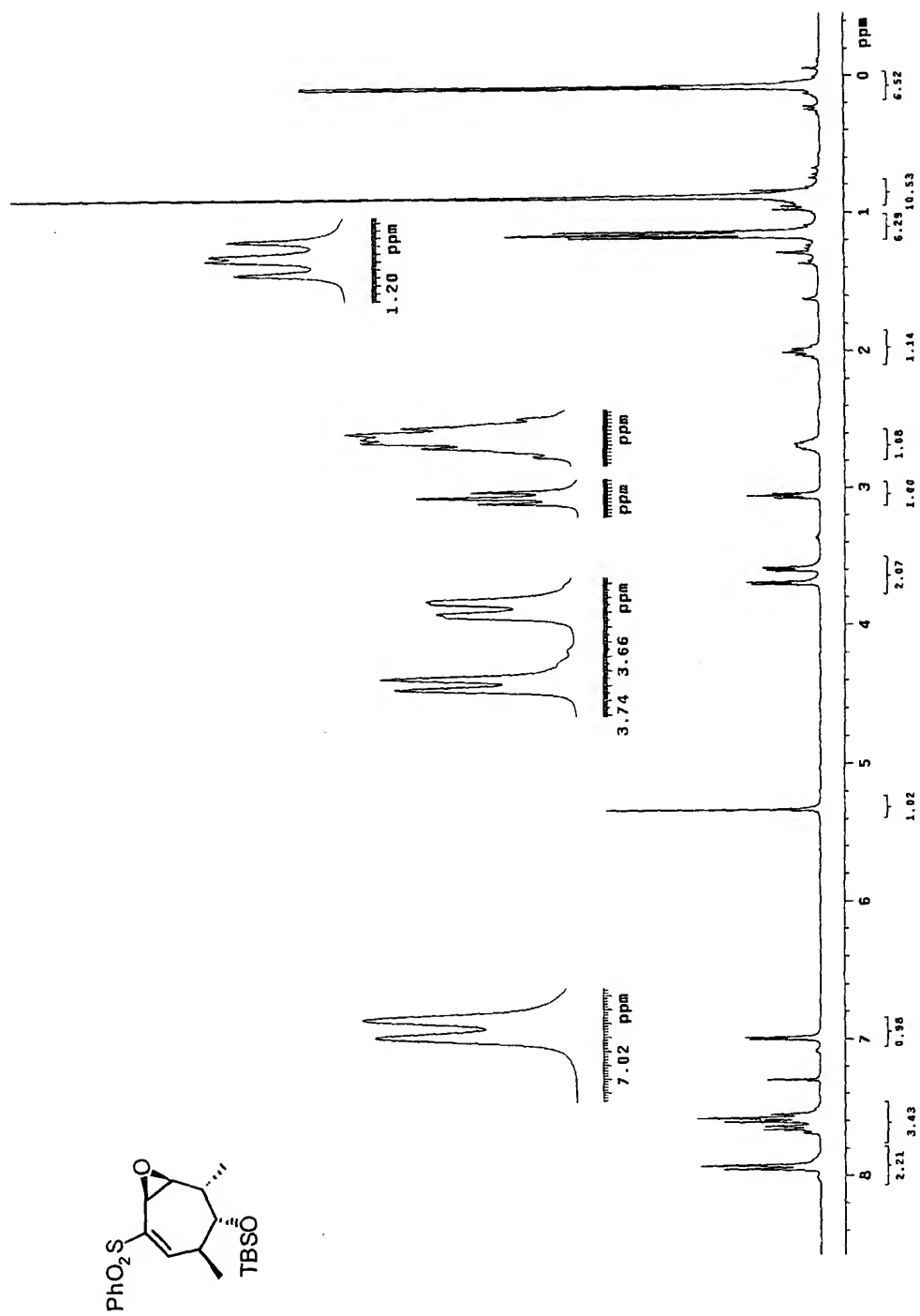
300MHz  $^1\text{H}$  NMR of compound  $\alpha 37$  in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



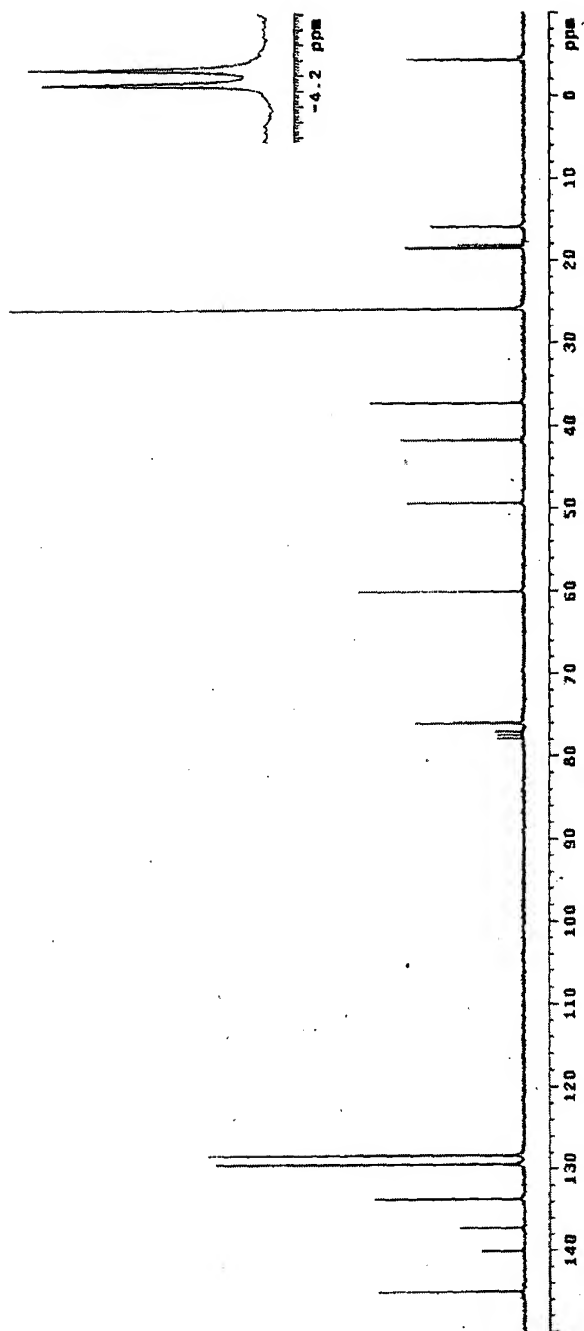
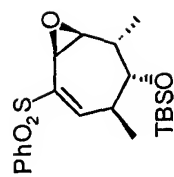
75MHz  $^{13}\text{C}$  NMR of compound  $\alpha 37$  in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



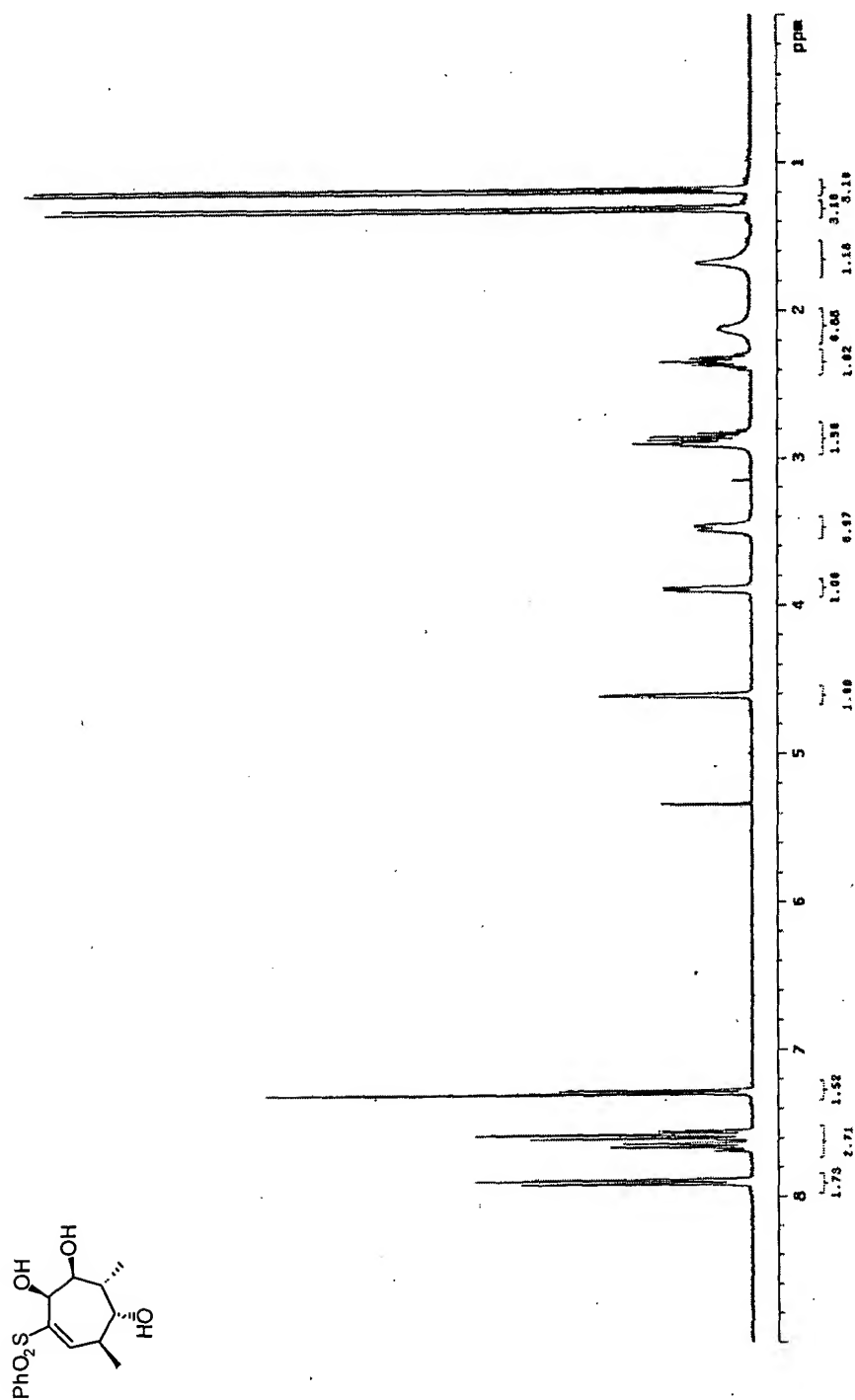
300MHz  $^1\text{H}$  NMR of compound  $\beta 37$  in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



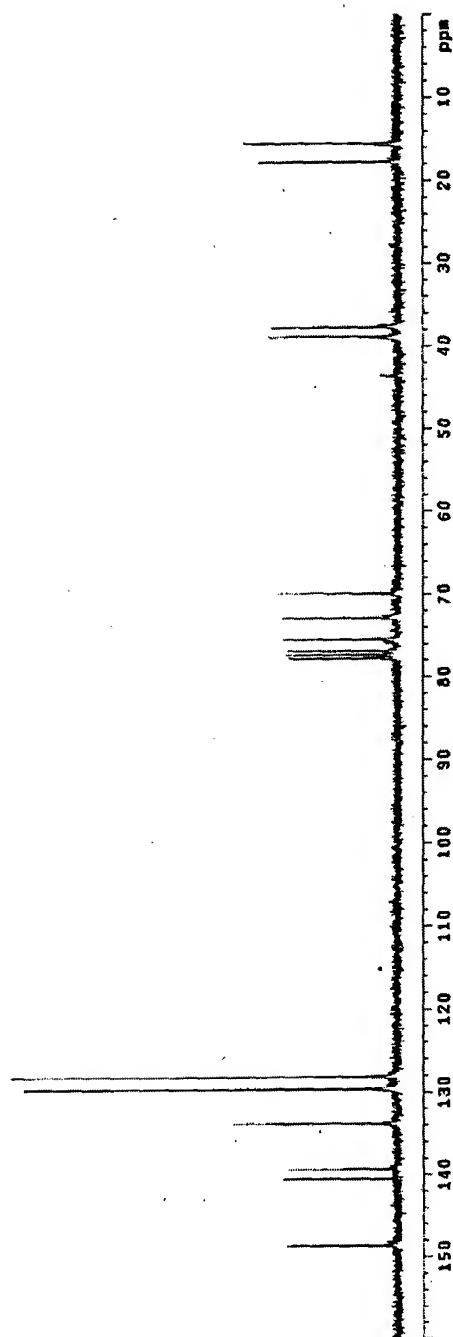
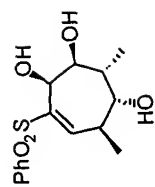
75MHz <sup>13</sup>C NMR of compound 337 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



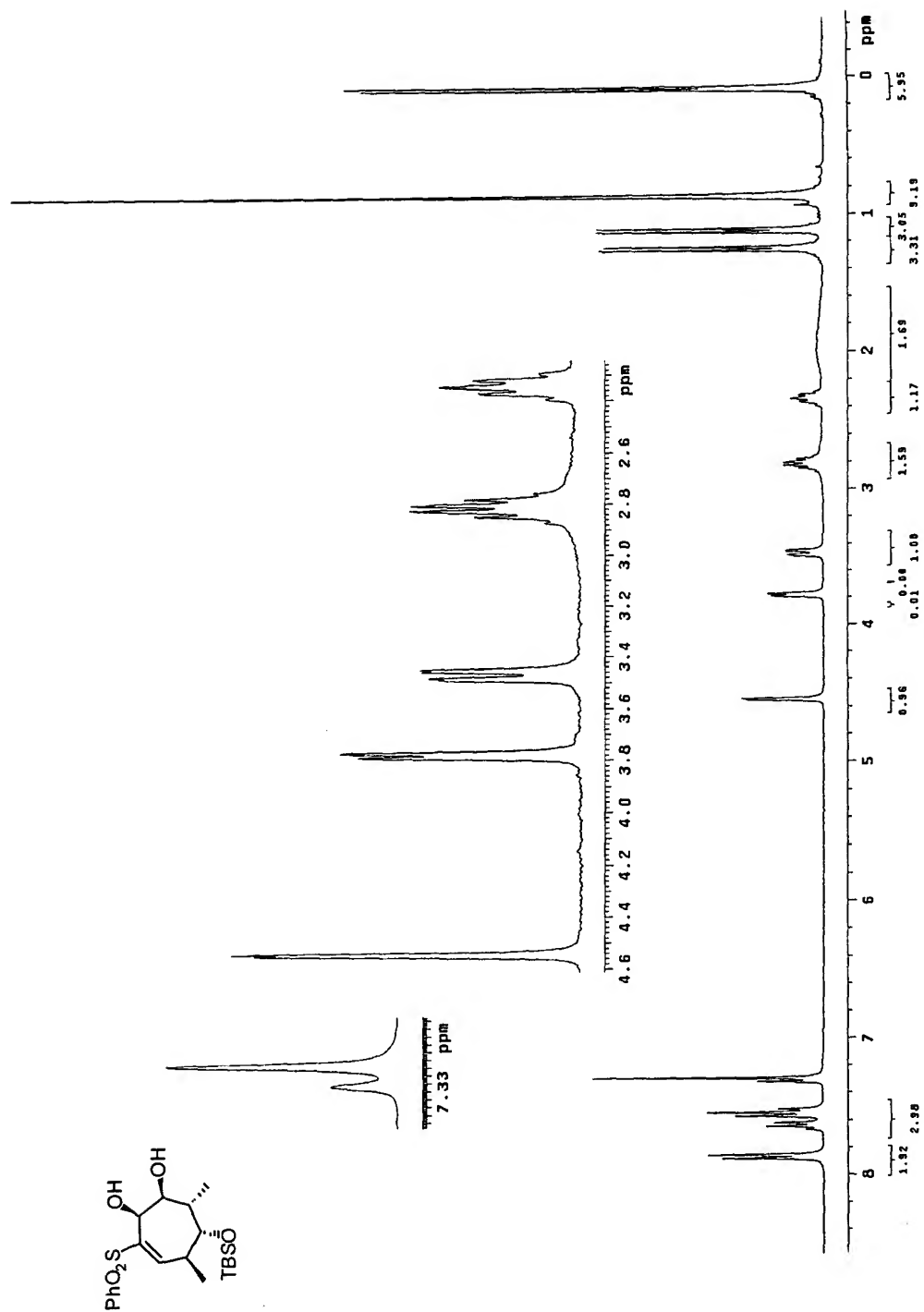
300MHz <sup>1</sup>H NMR of compound 38 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



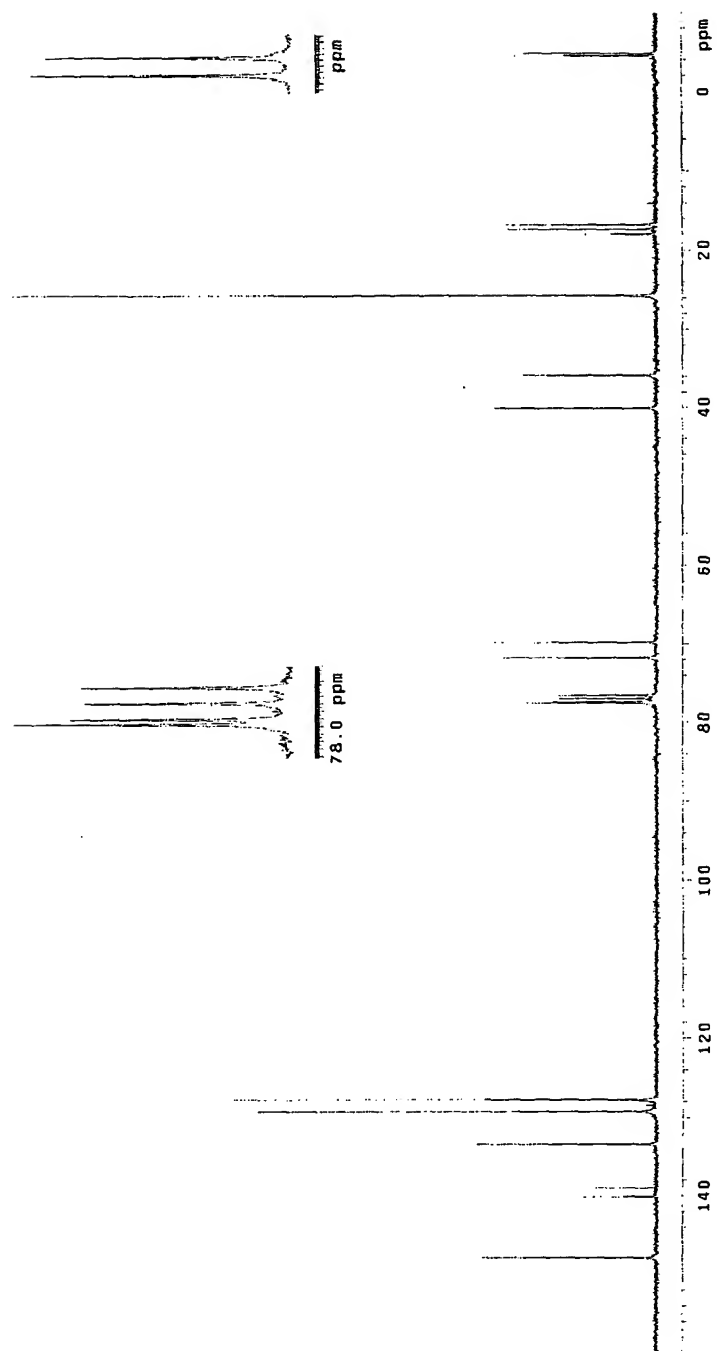
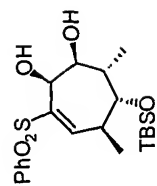
75MHz <sup>13</sup>C NMR of compound 38 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



300MHz  $^1\text{H}$  NMR of compound 39 in  $\text{CDCl}_3$

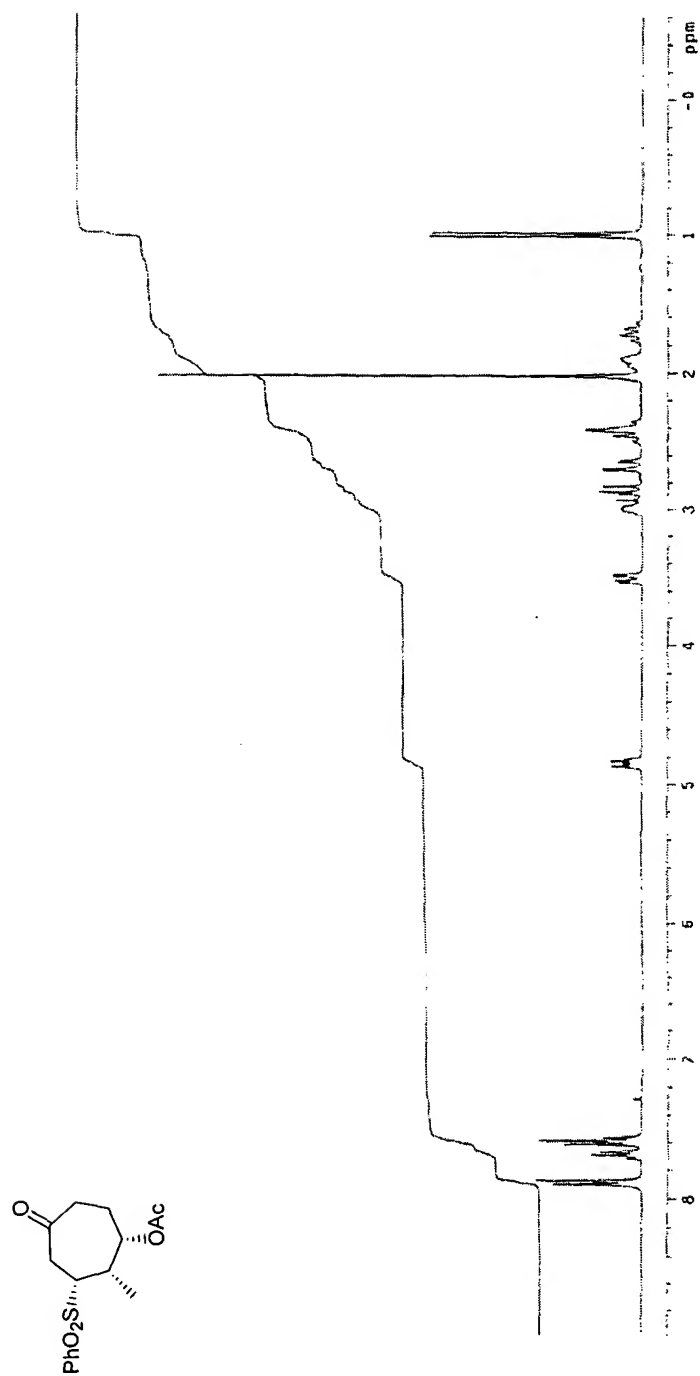
FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 39 in  $\text{CDCl}_3$

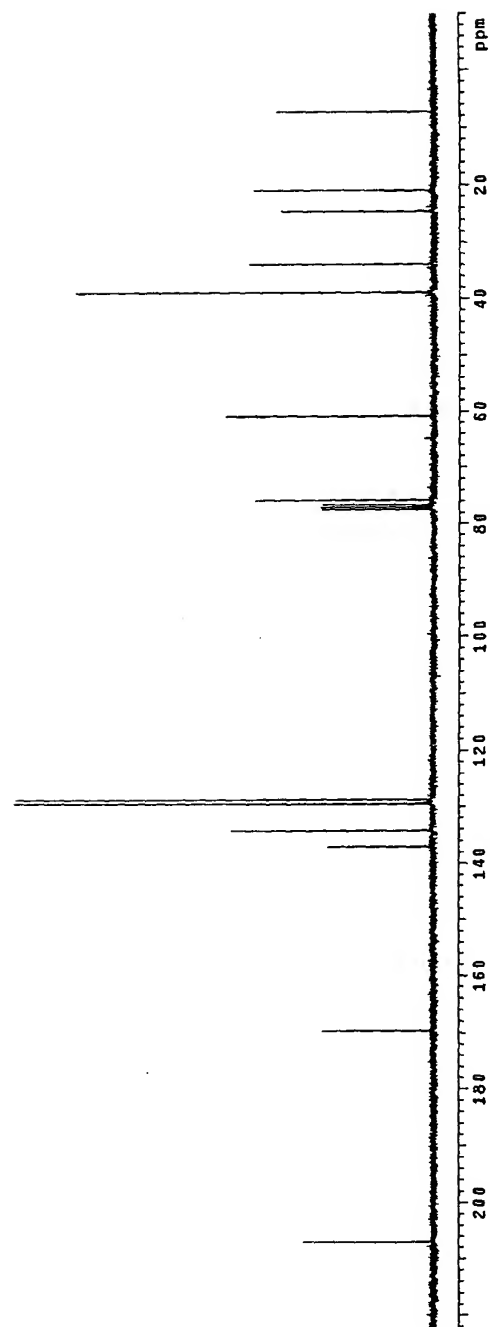
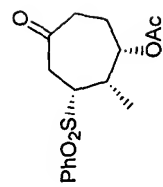


FIGURE 8 (Cont'd)



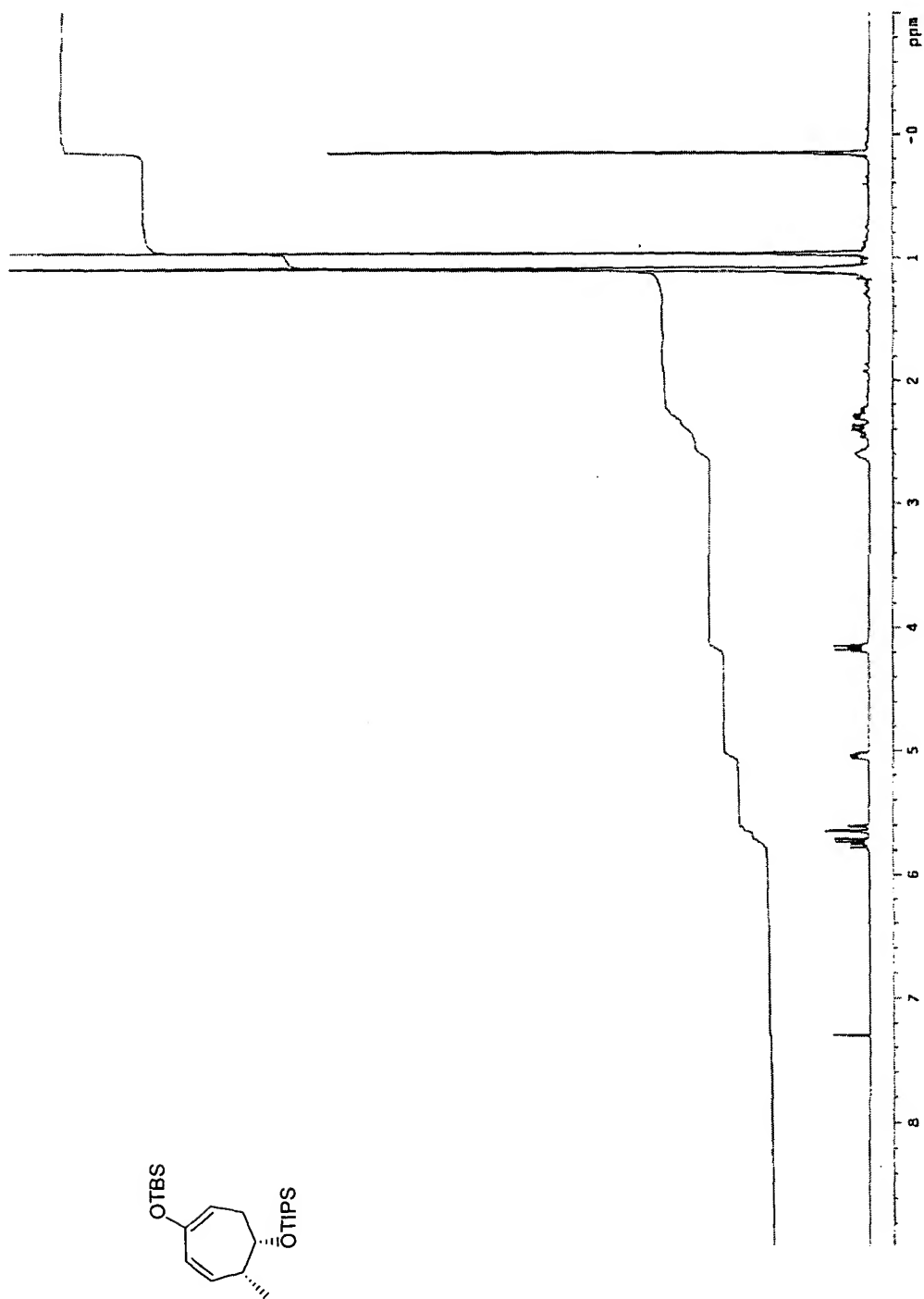
300MHz  $^1\text{H}$  NMR of compound 41 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



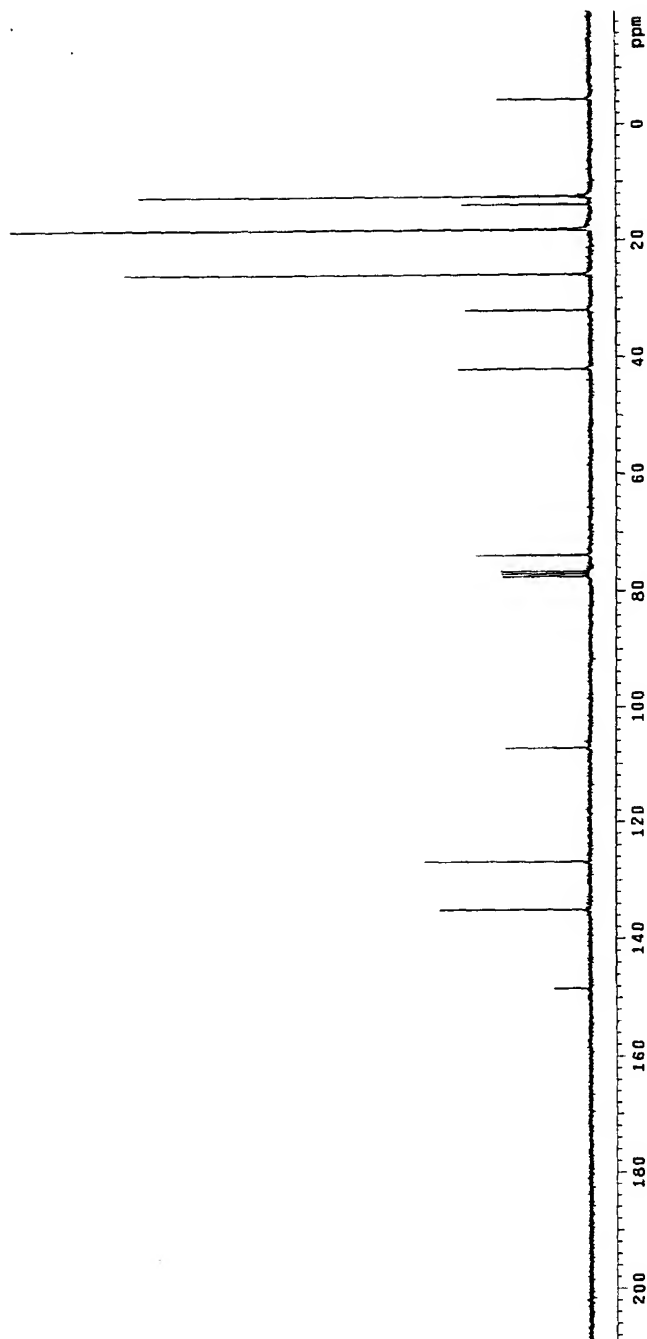
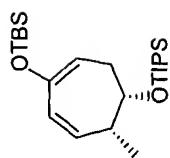
75MHz <sup>13</sup>C NMR of compound 41 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



300MHz <sup>1</sup>H NMR of compound 42 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 42 in  $\text{CDCl}_3$

Chemical structure of the compound is shown below:

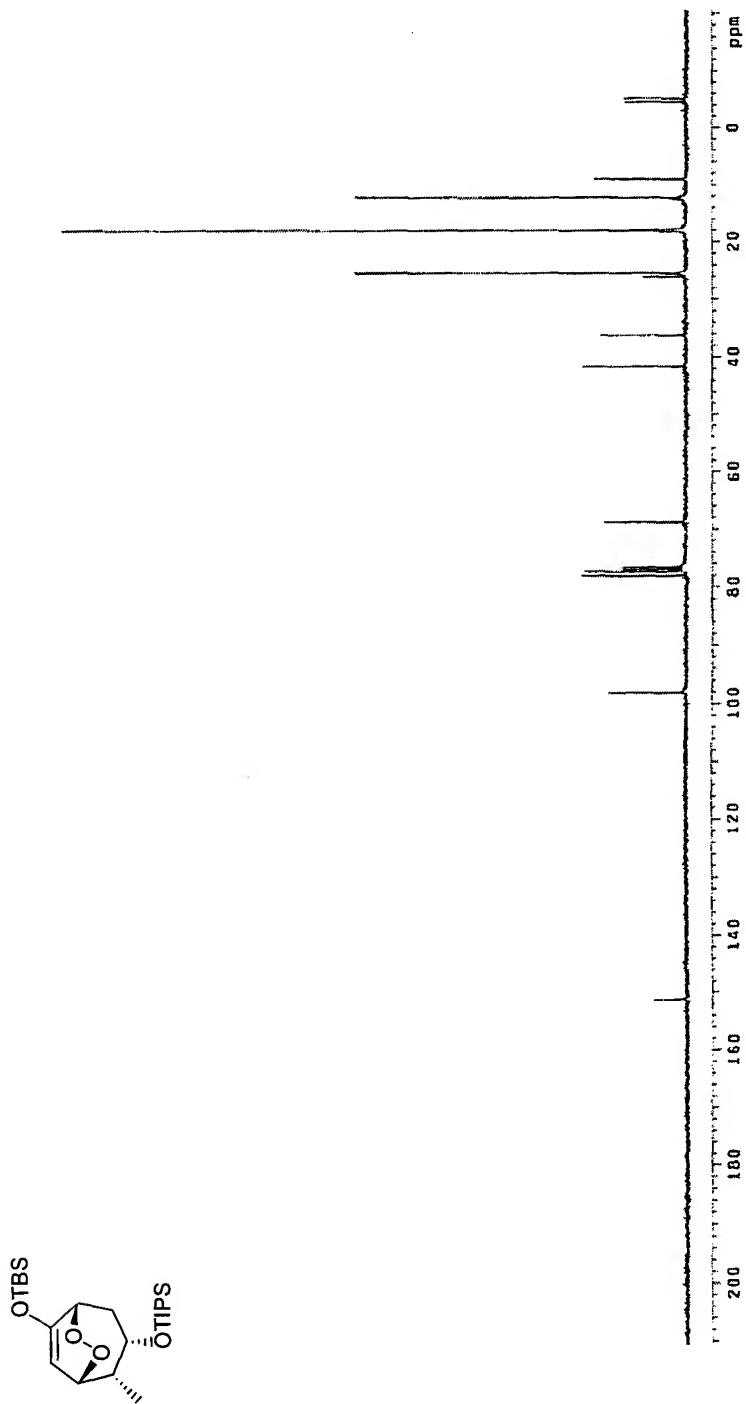
C1=CC(=C(C=C1)C2=CC=CC=C2)C3=CC=CC=C3

The structure is a 1,3,5-trisubstituted benzene ring. The substituents are:

- A phenyl group (C<sub>6</sub>H<sub>5</sub>) at position 1.
- A phenyl group (C<sub>6</sub>H<sub>5</sub>) at position 3.
- A phenyl group (C<sub>6</sub>H<sub>5</sub>) at position 5.

300MHz  $^1\text{H}$  NMR of compound 43 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 43 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)

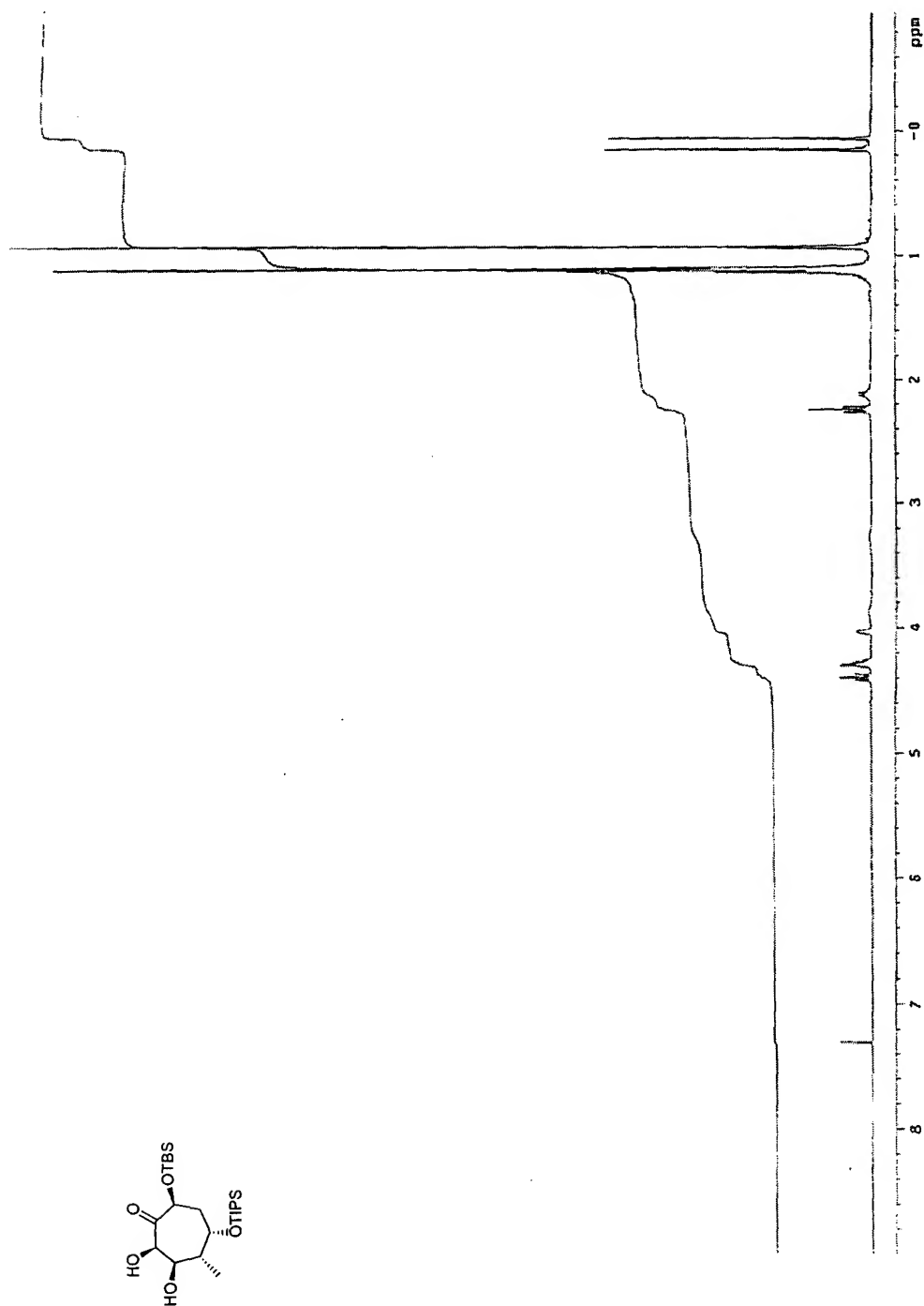
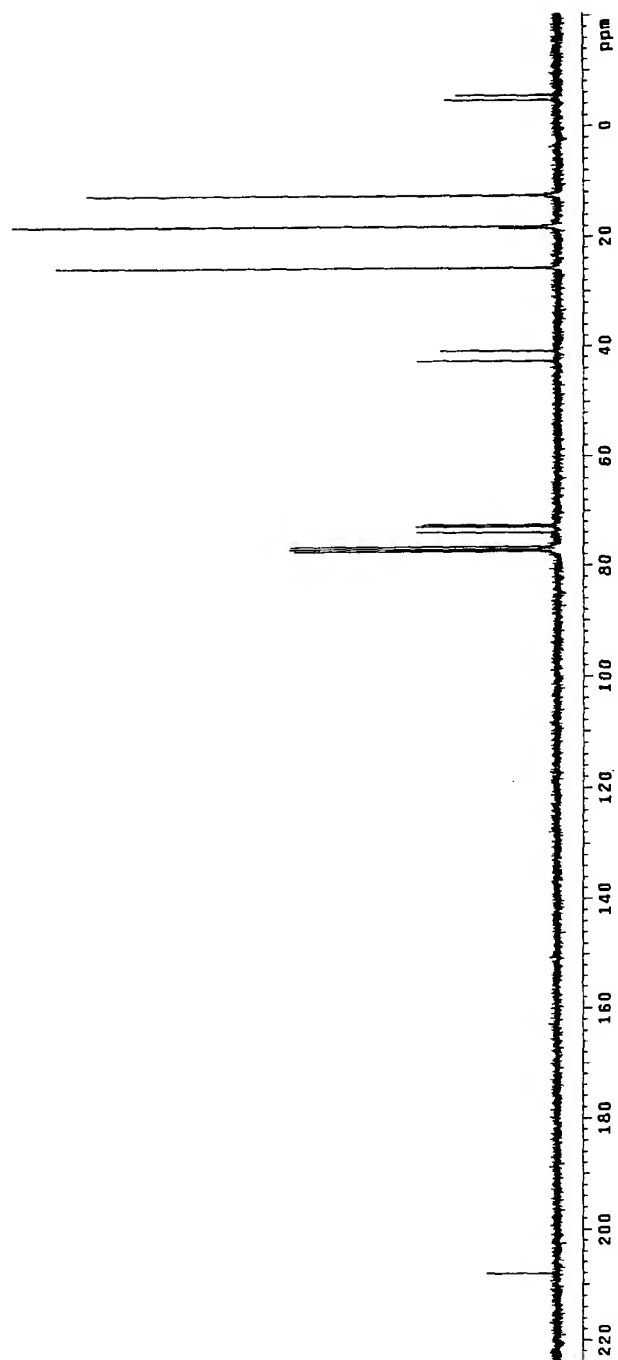
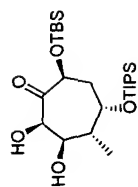


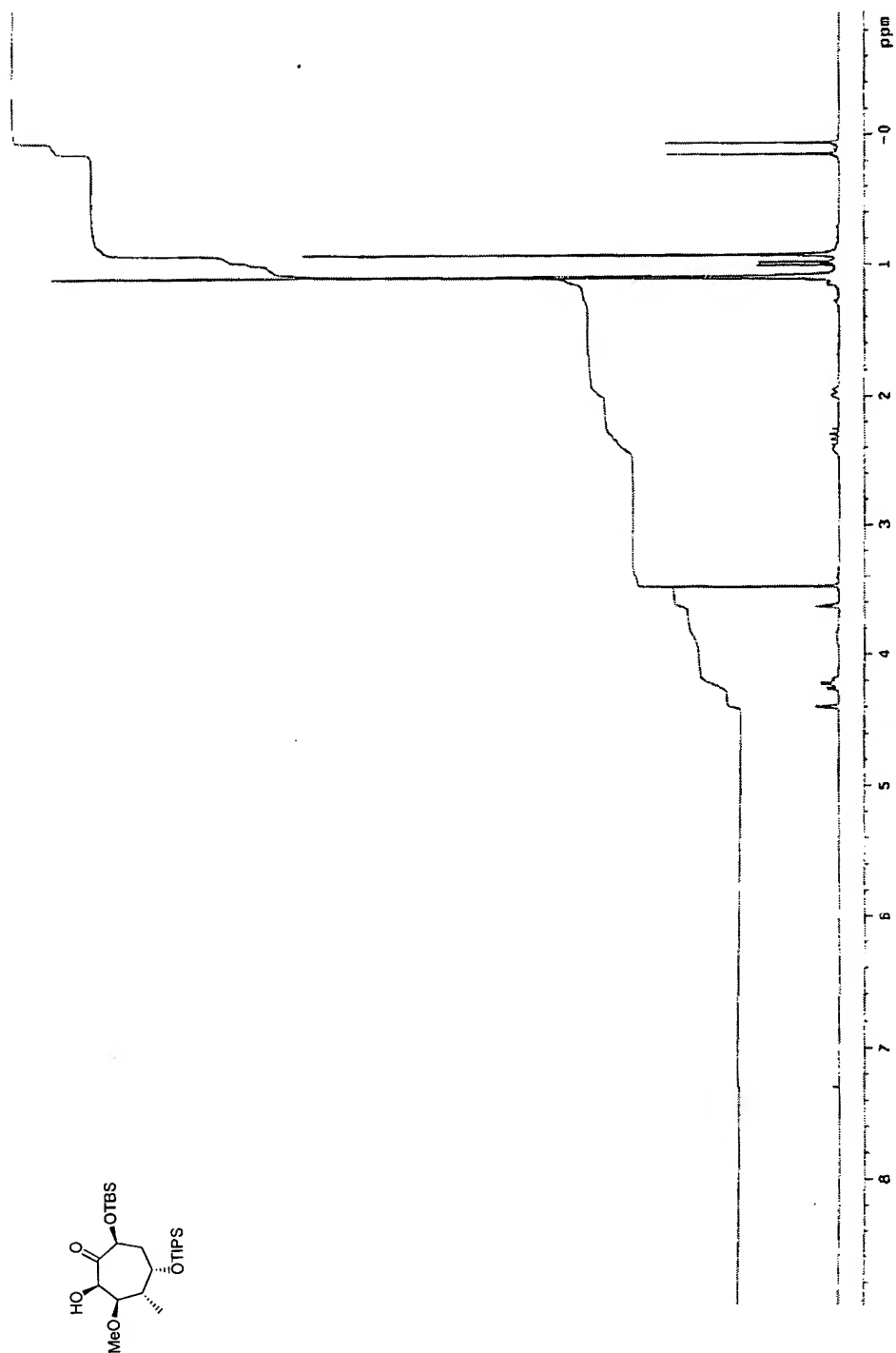
FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 46 in  $\text{CDCl}_3$

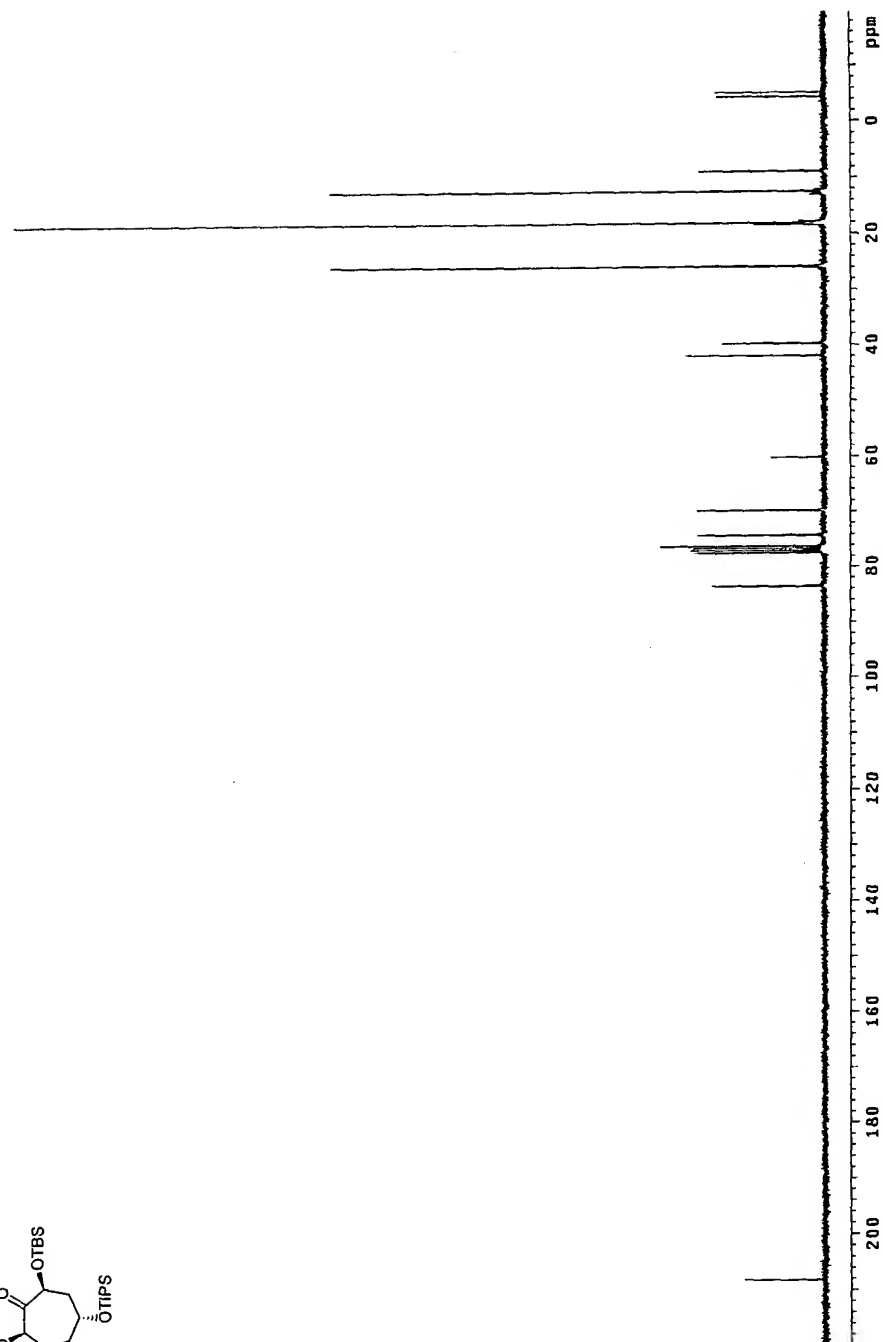
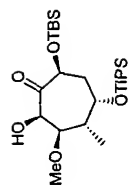


FIGURE 8 (Cont'd)



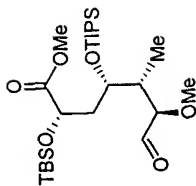
300MHz <sup>1</sup>H NMR of compound 47 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 47 in  $\text{CDCl}_3$

**FIGURE 8 (Cont'd)**

300MHz <sup>1</sup>H NMR of compound 48 in CDCl<sub>3</sub>

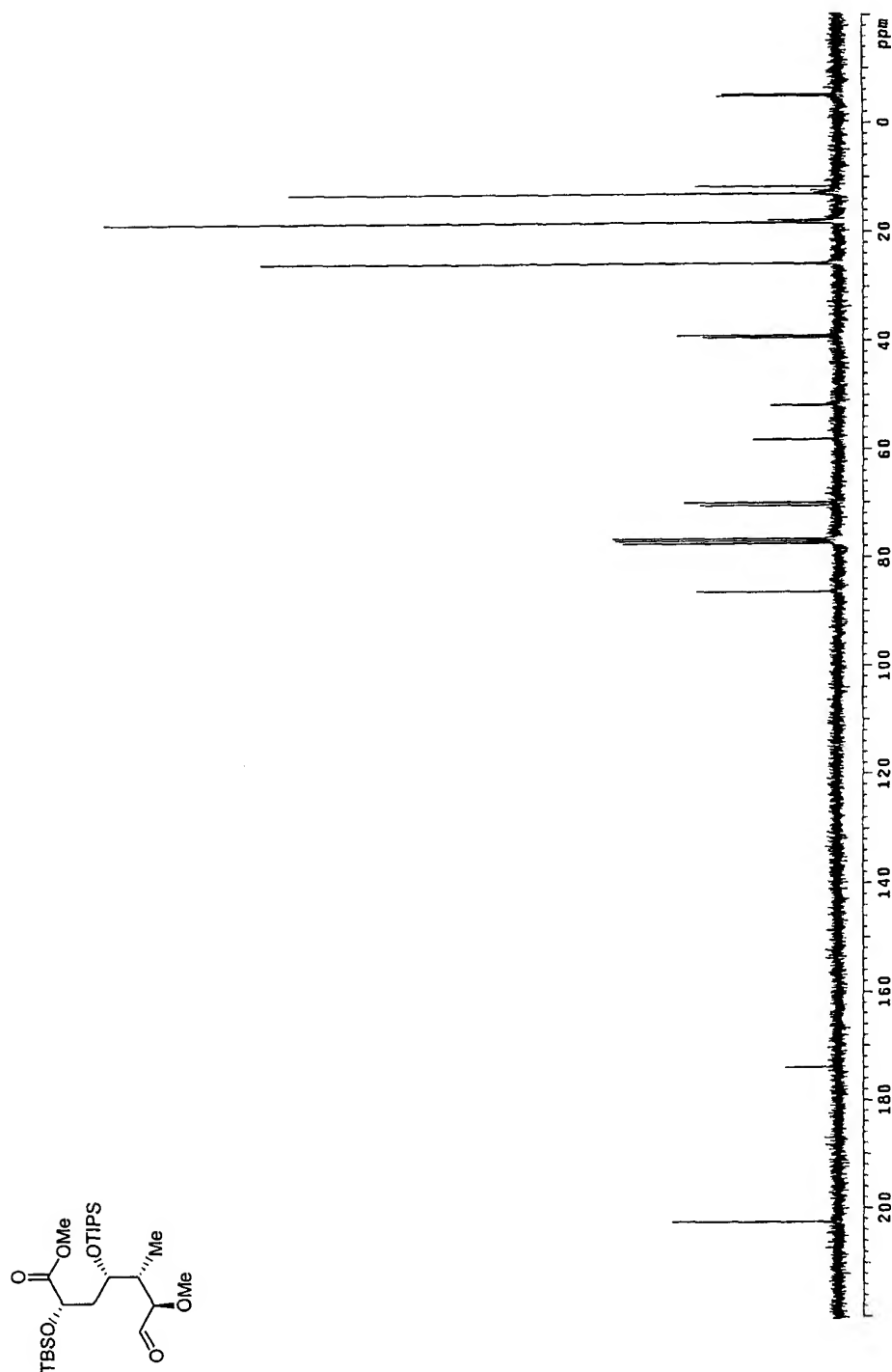
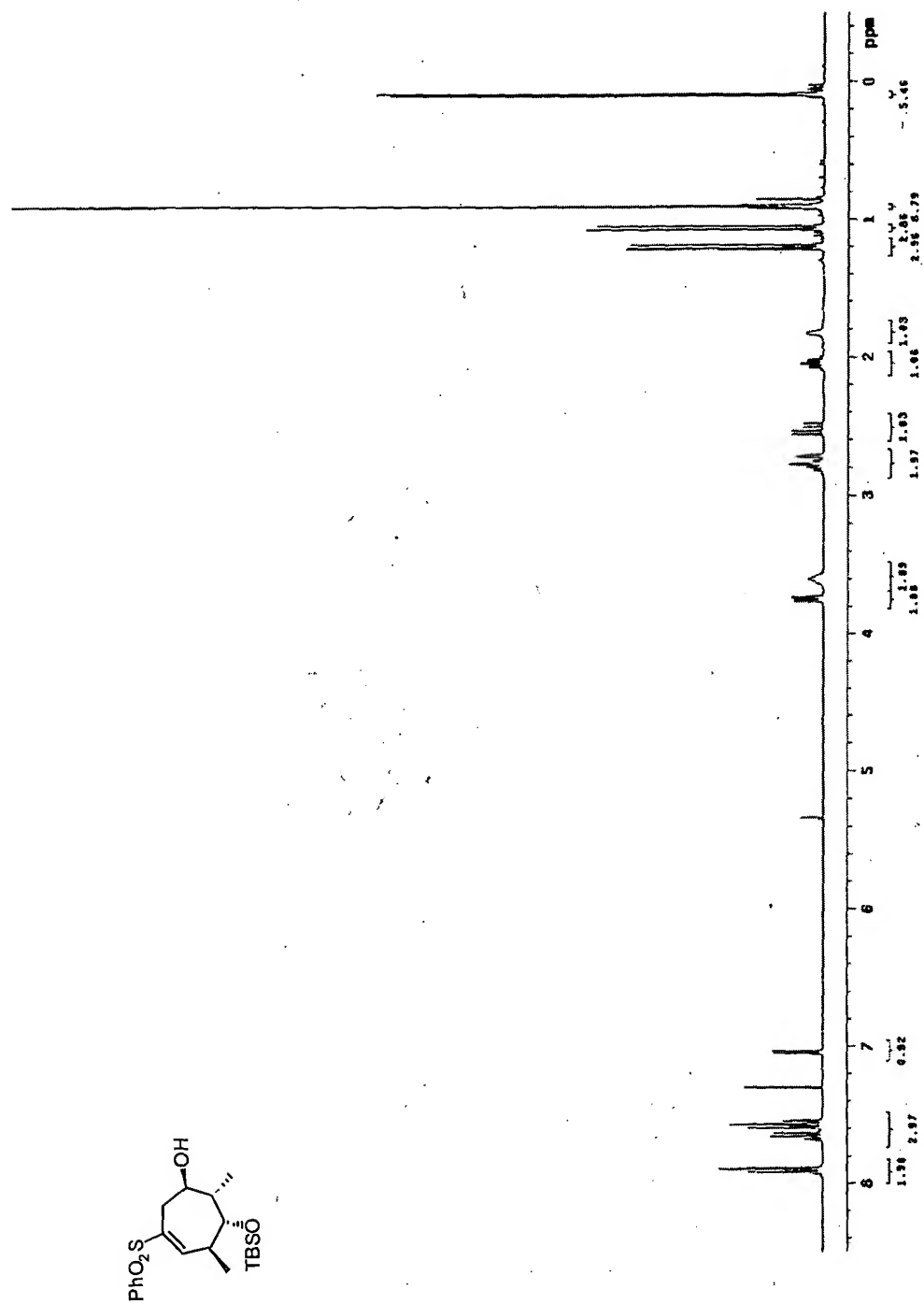
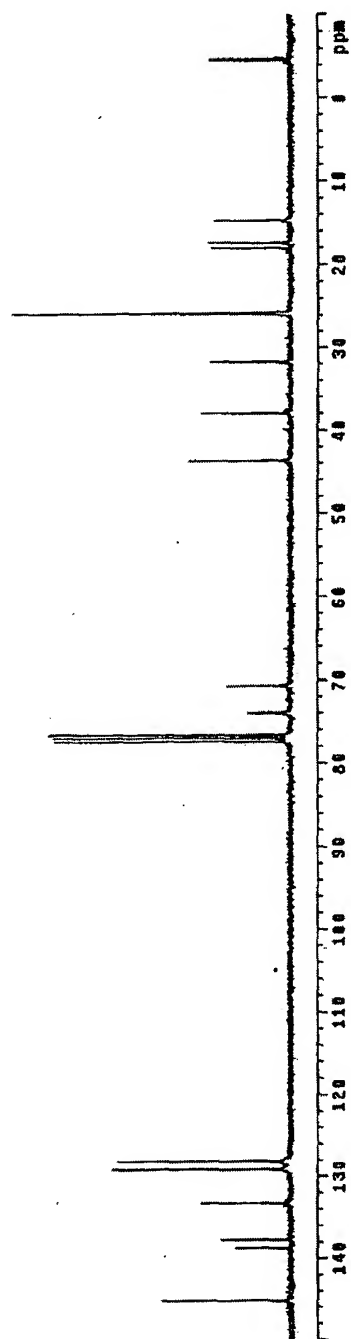
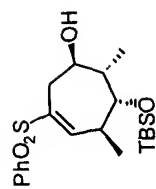
75MHz  $^{13}\text{C}$  NMR of compound 48 in  $\text{CDCl}_3$ 

FIGURE 8 (Cont'd)



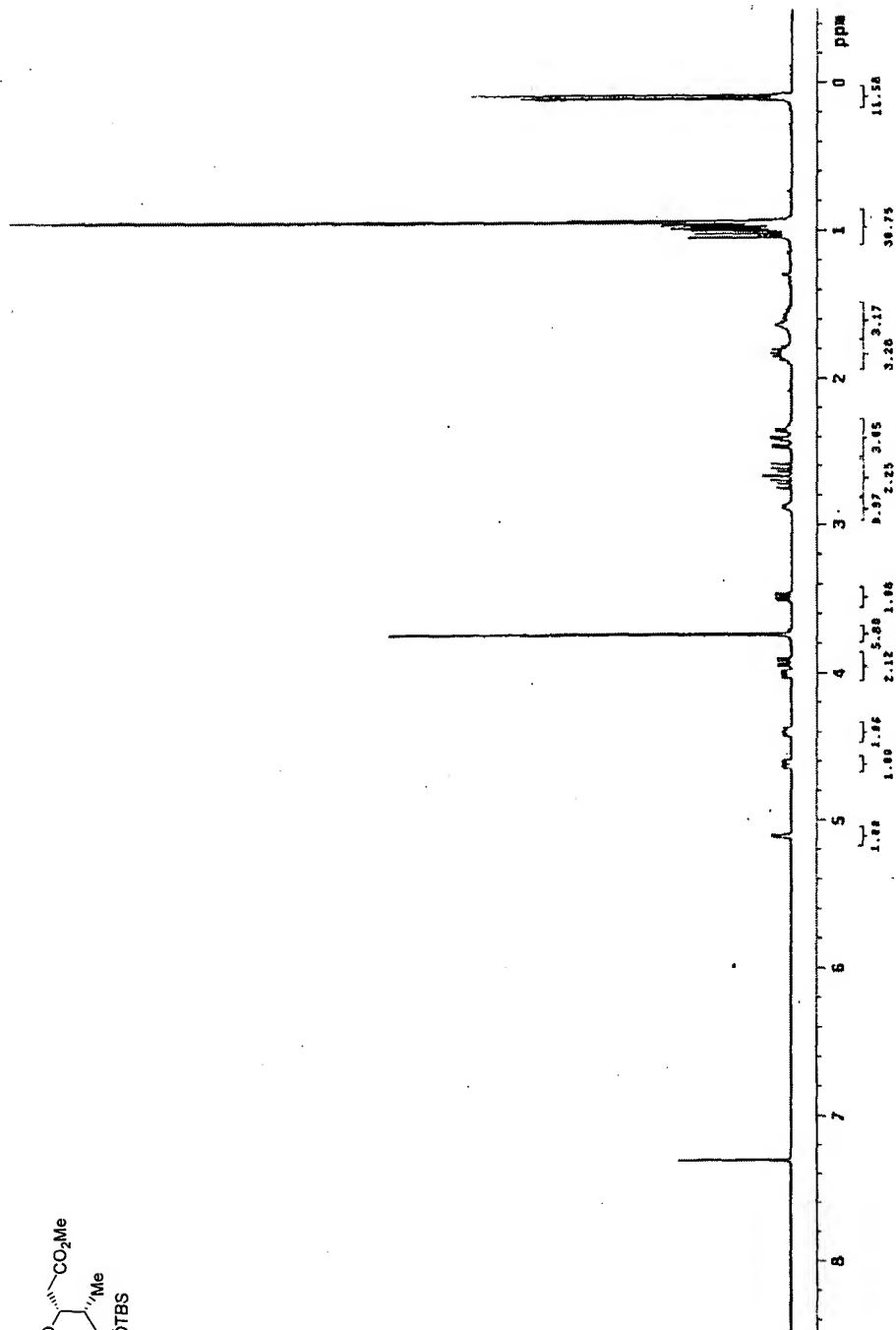
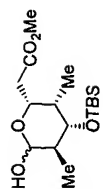
300MHz  $^1\text{H}$  NMR of compound 56 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



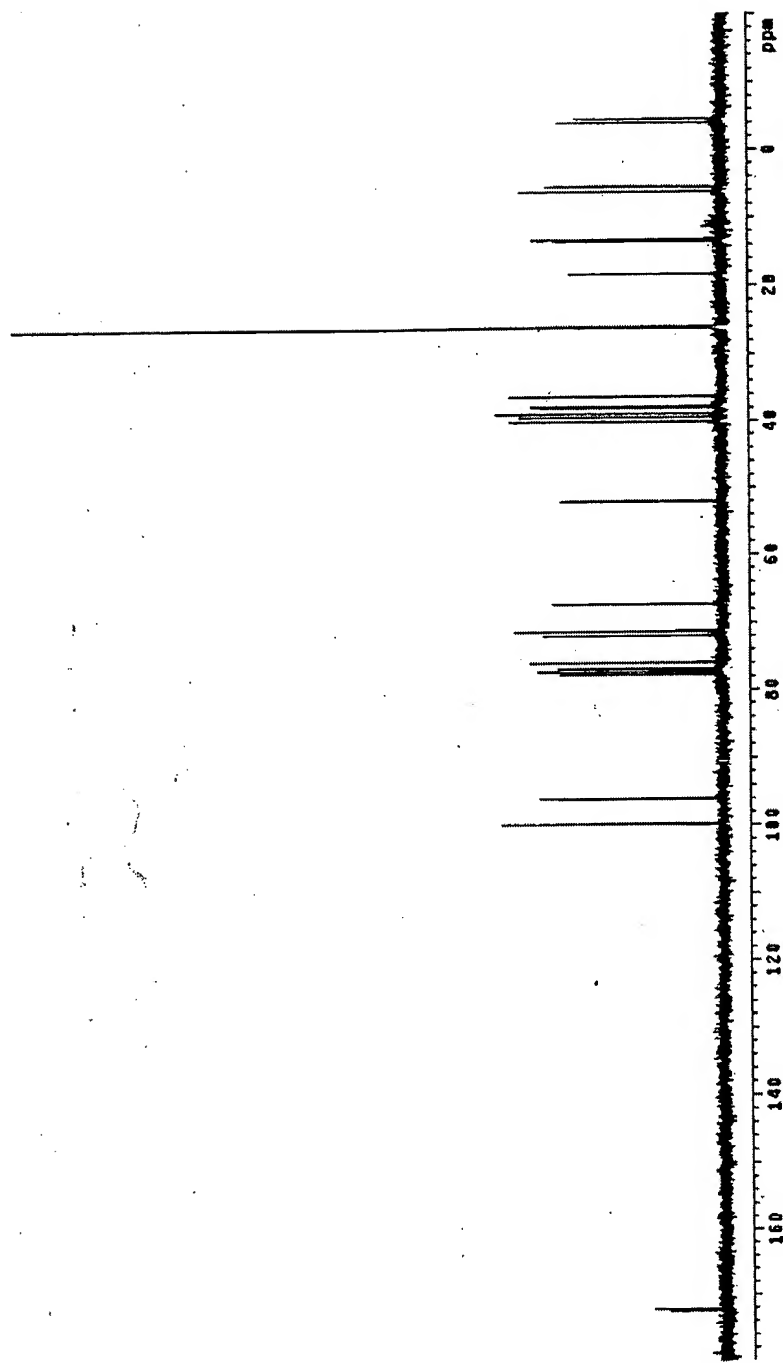
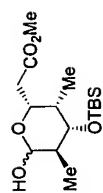
75MHz <sup>13</sup>C NMR of compound 56 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



300MHz  $^1\text{H}$  NMR of compound 57 in  $\text{CDCl}_3$

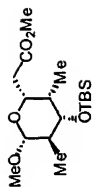
FIGURE 8 (Cont'd)



75MHz <sup>13</sup>C NMR of compound 57 in CDCl<sub>3</sub>

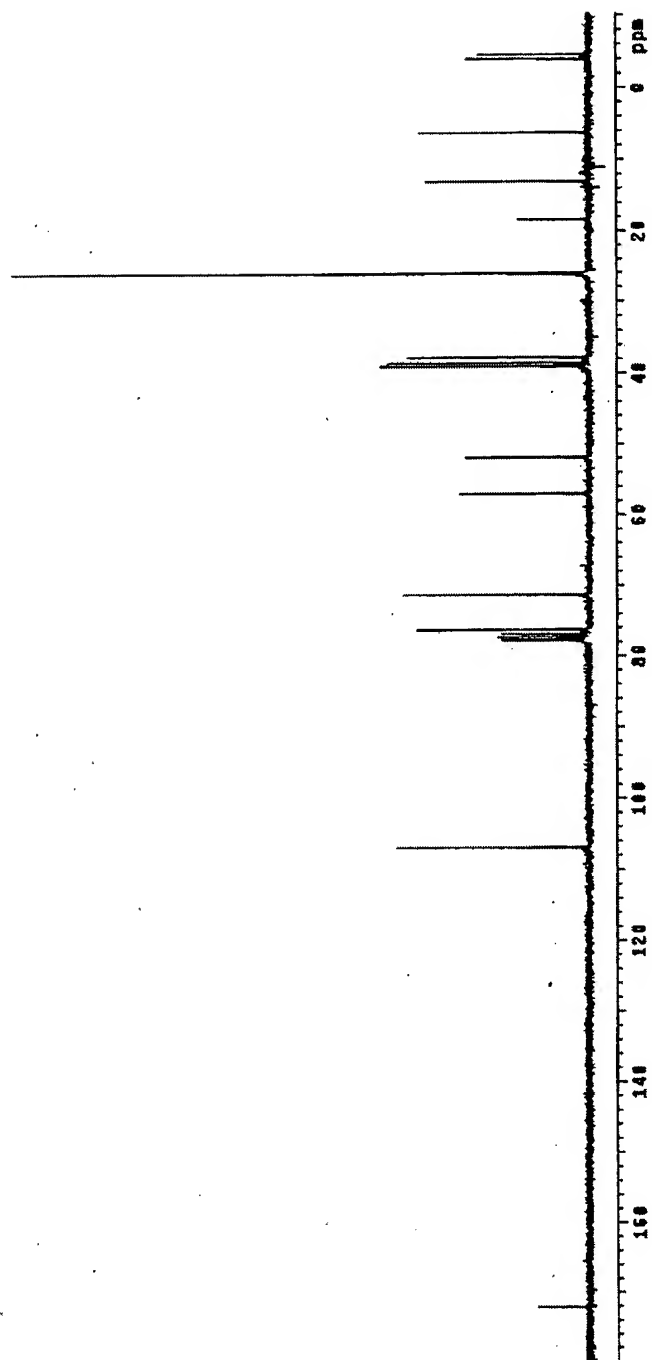
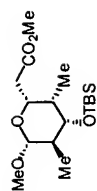


**FIGURE 8 (Cont'd)**



300MHz  $^1\text{H}$  NMR of compound **58a** in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



**FIGURE 8 (Cont'd)**

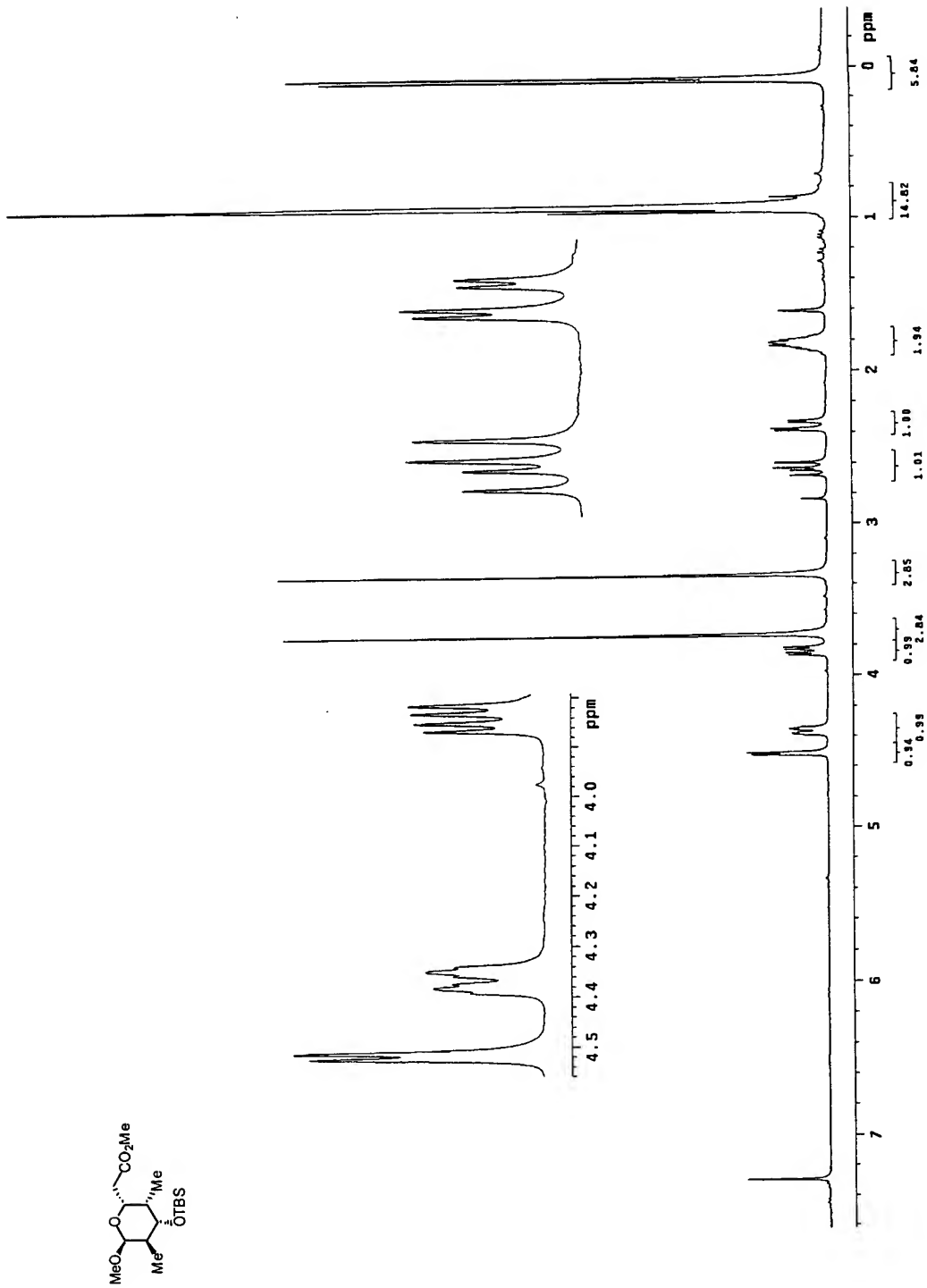
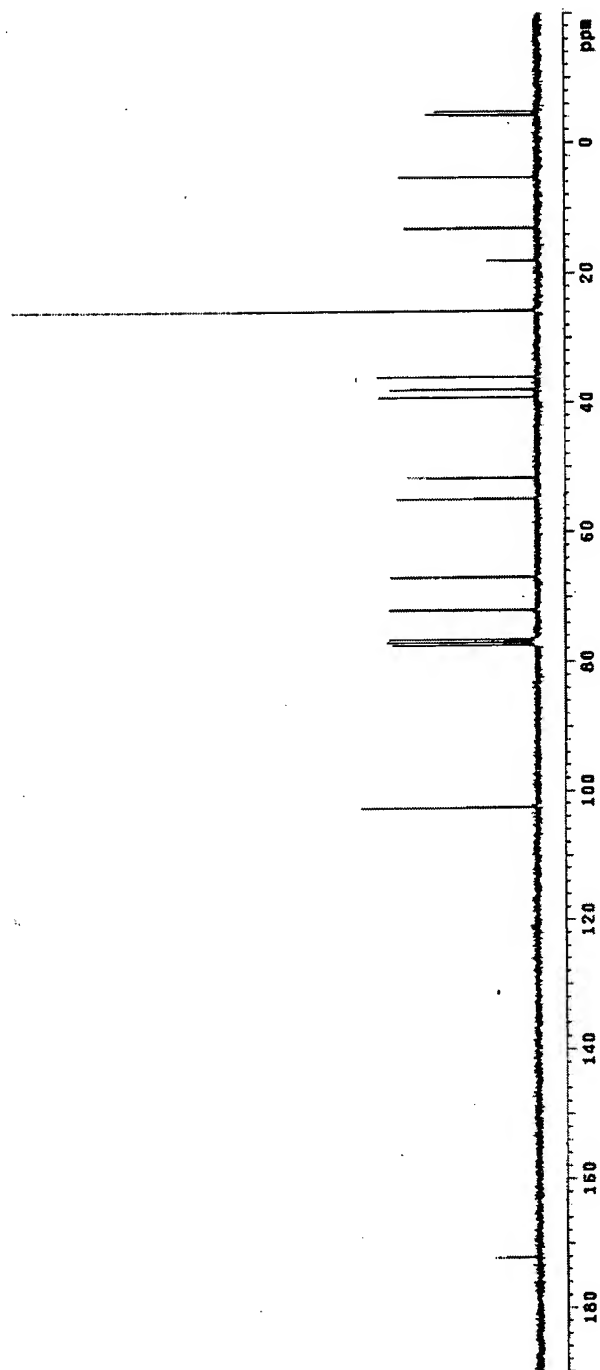
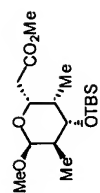
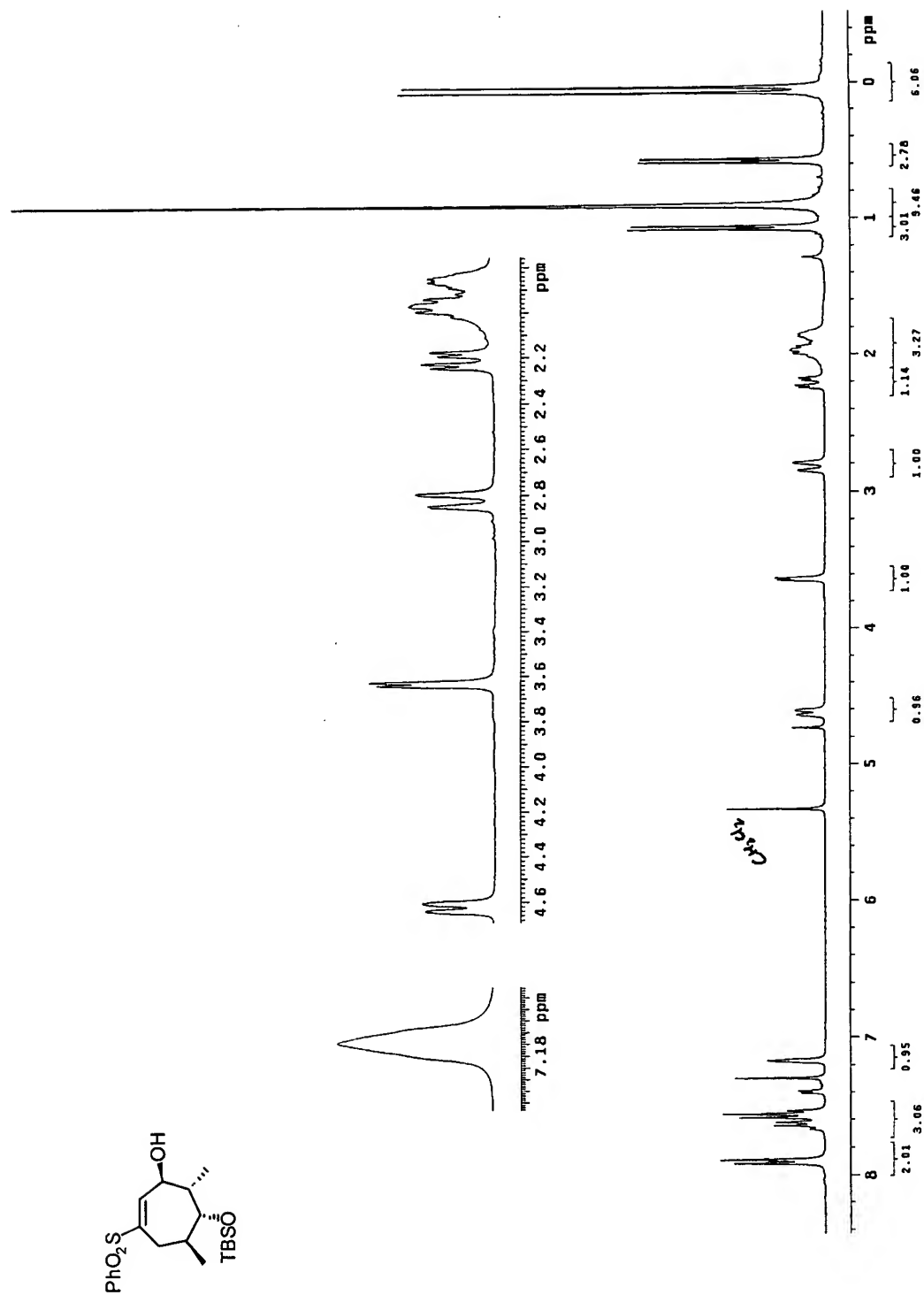
300MHz <sup>1</sup>H NMR of compound 58β in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)

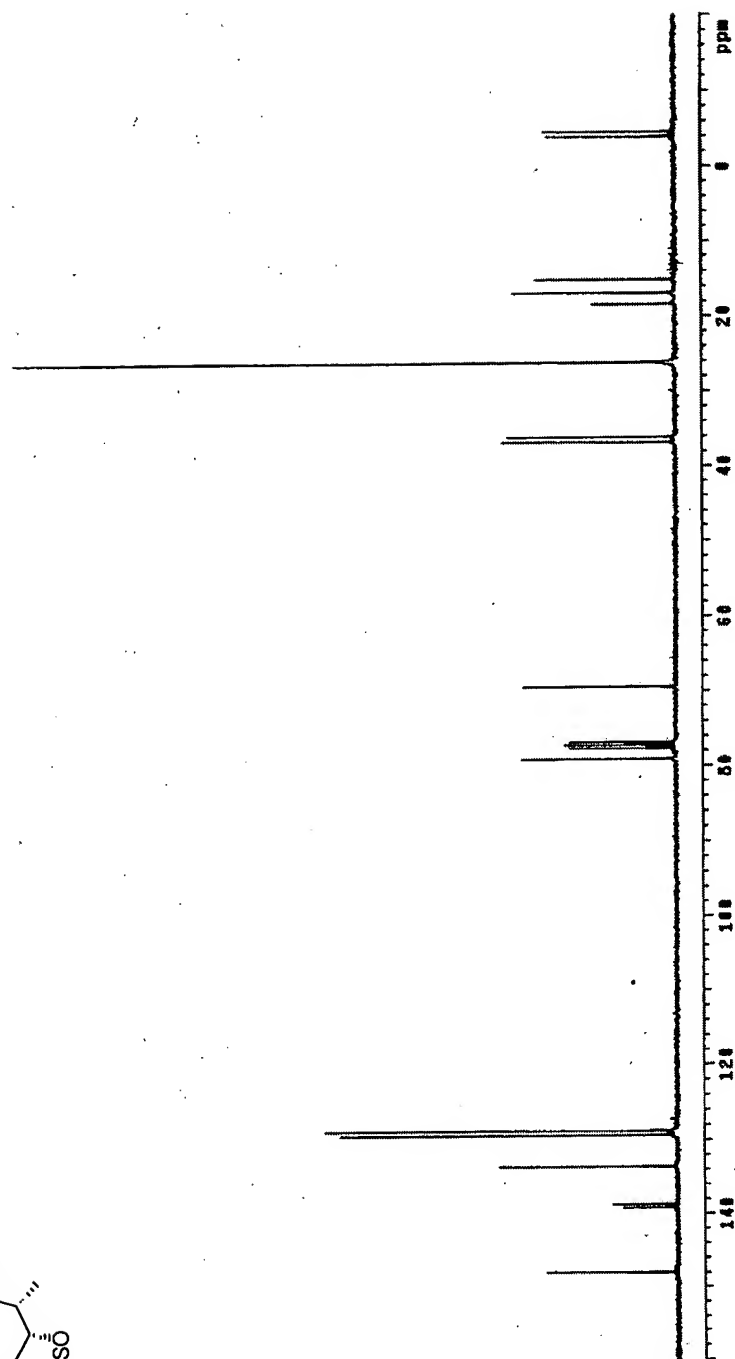


75MHz  $^{13}\text{C}$  NMR of compound 58 $\beta$  in  $\text{CDCl}_3$

**FIGURE 8 (Cont'd)**

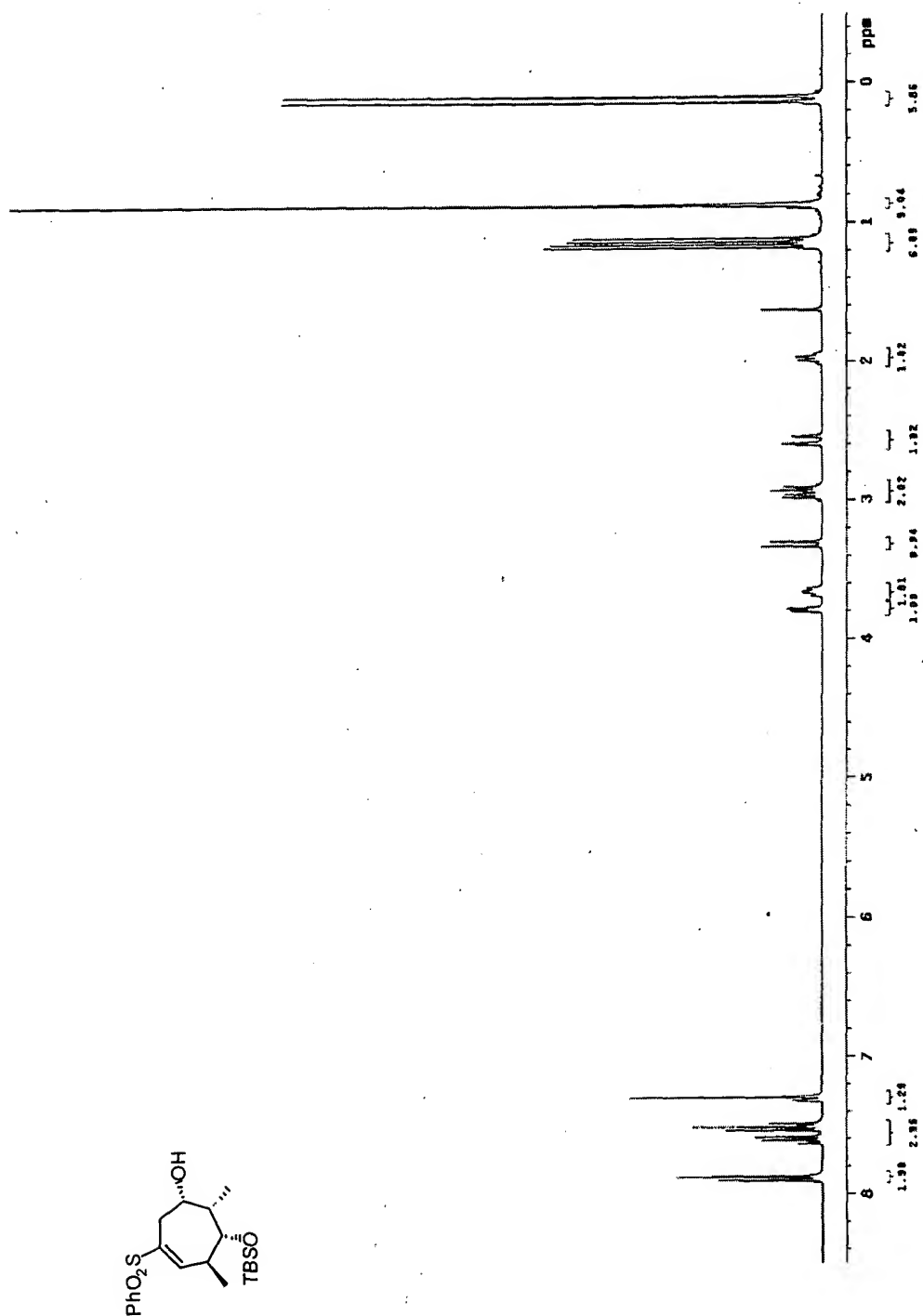


300MHz  $^1\text{H}$  NMR of compound 59 in  $\text{CDCl}_3$



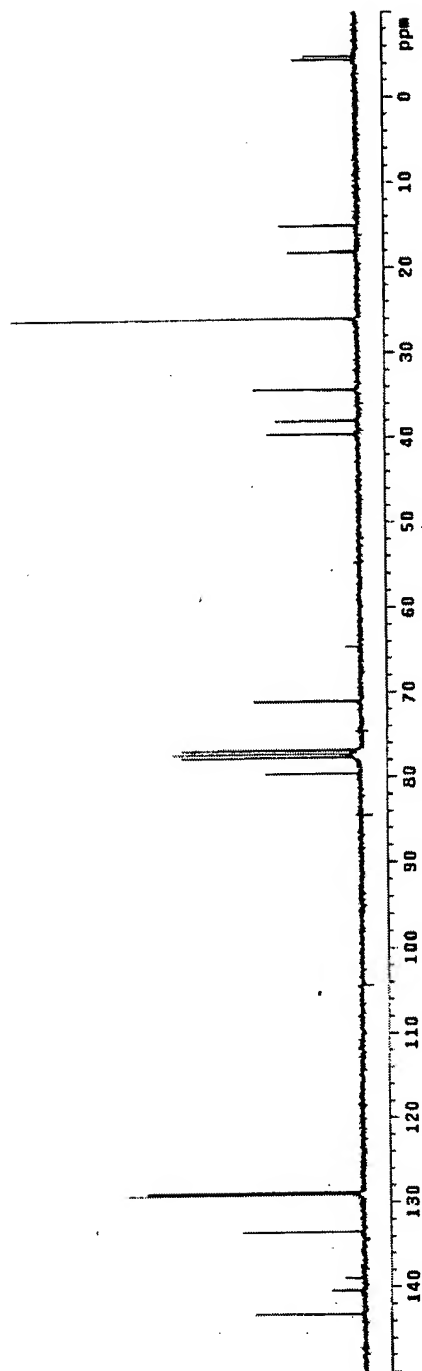
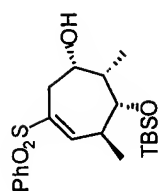
75MHz  $^{13}\text{C}$  NMR of compound 59 in  $\text{CDCl}_3$

**FIGURE 8 (Cont'd)**



300MHz  $^1\text{H}$  NMR of compound 60 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



75MHz <sup>13</sup>C NMR of compound 60 in CDCl<sub>3</sub>



**FIGURE 8 (Cont'd)**

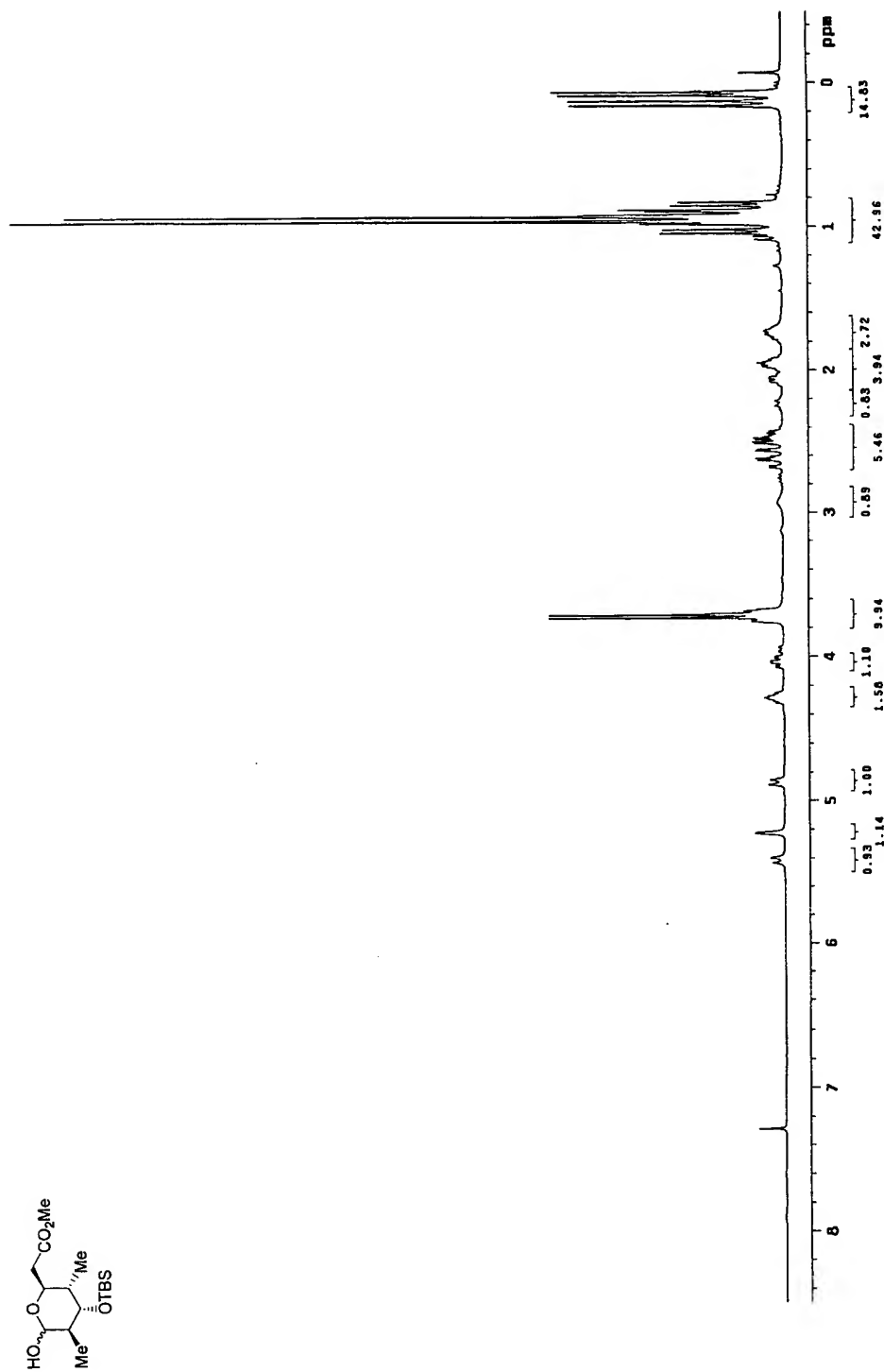
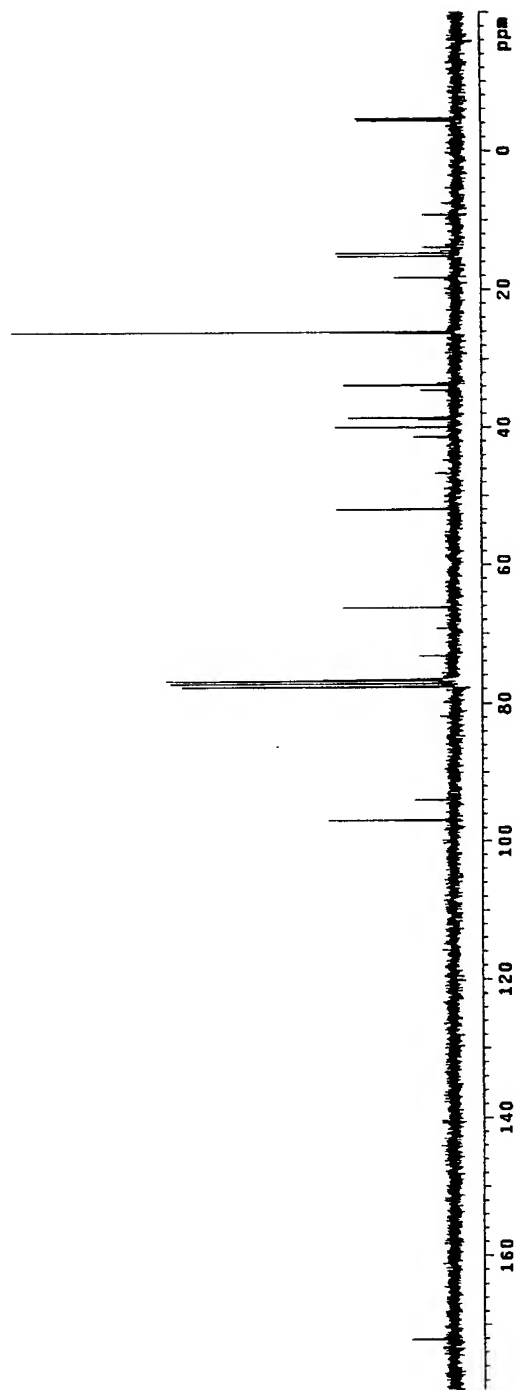
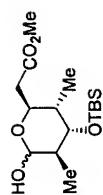
300MHz <sup>1</sup>H NMR of compound 61 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



75MHz <sup>13</sup>C NMR of compound 61 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)

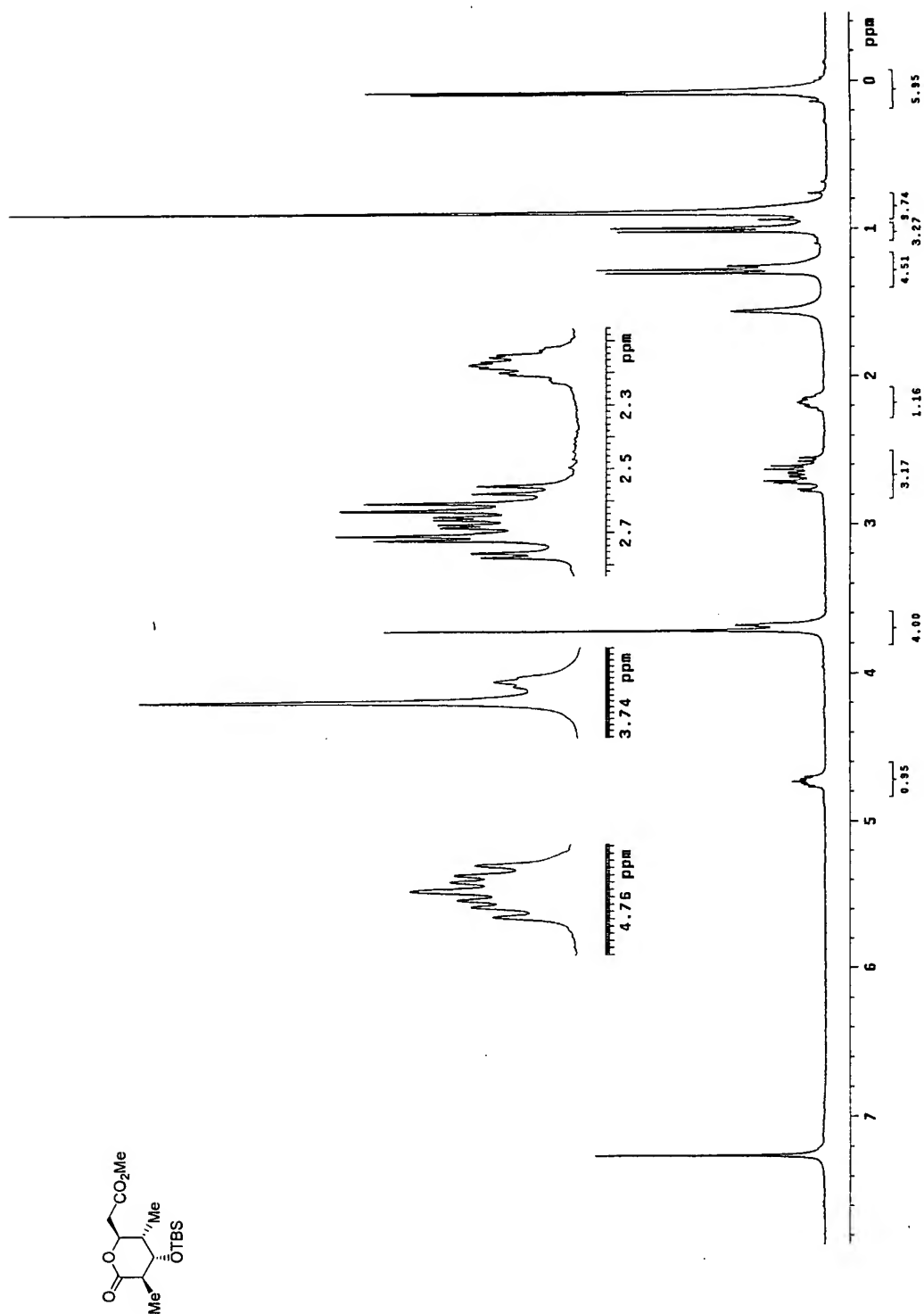
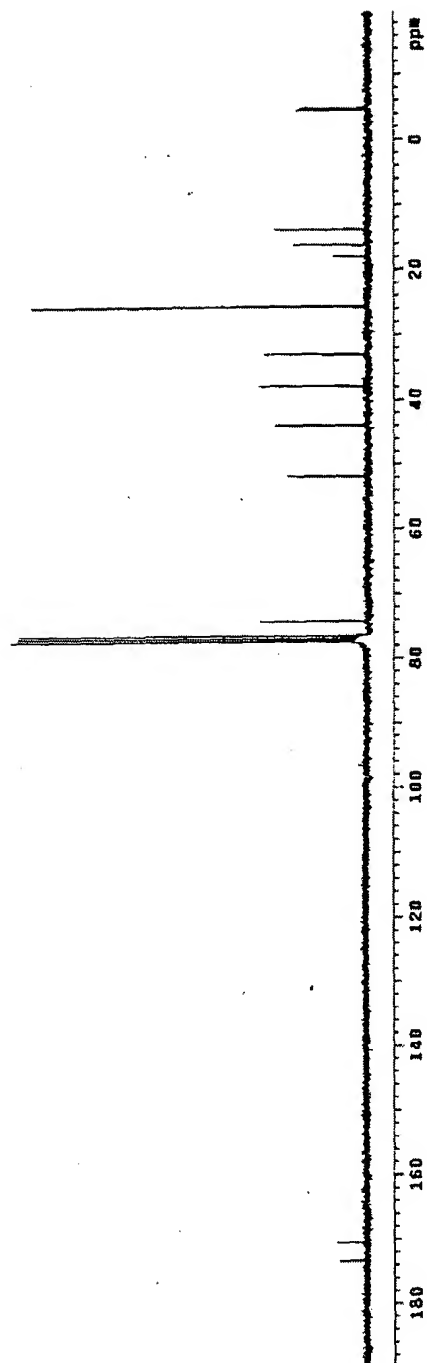
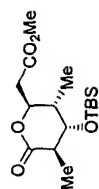


FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 62 in  $\text{CDCl}_3$

of

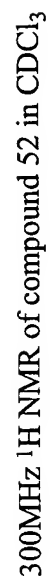
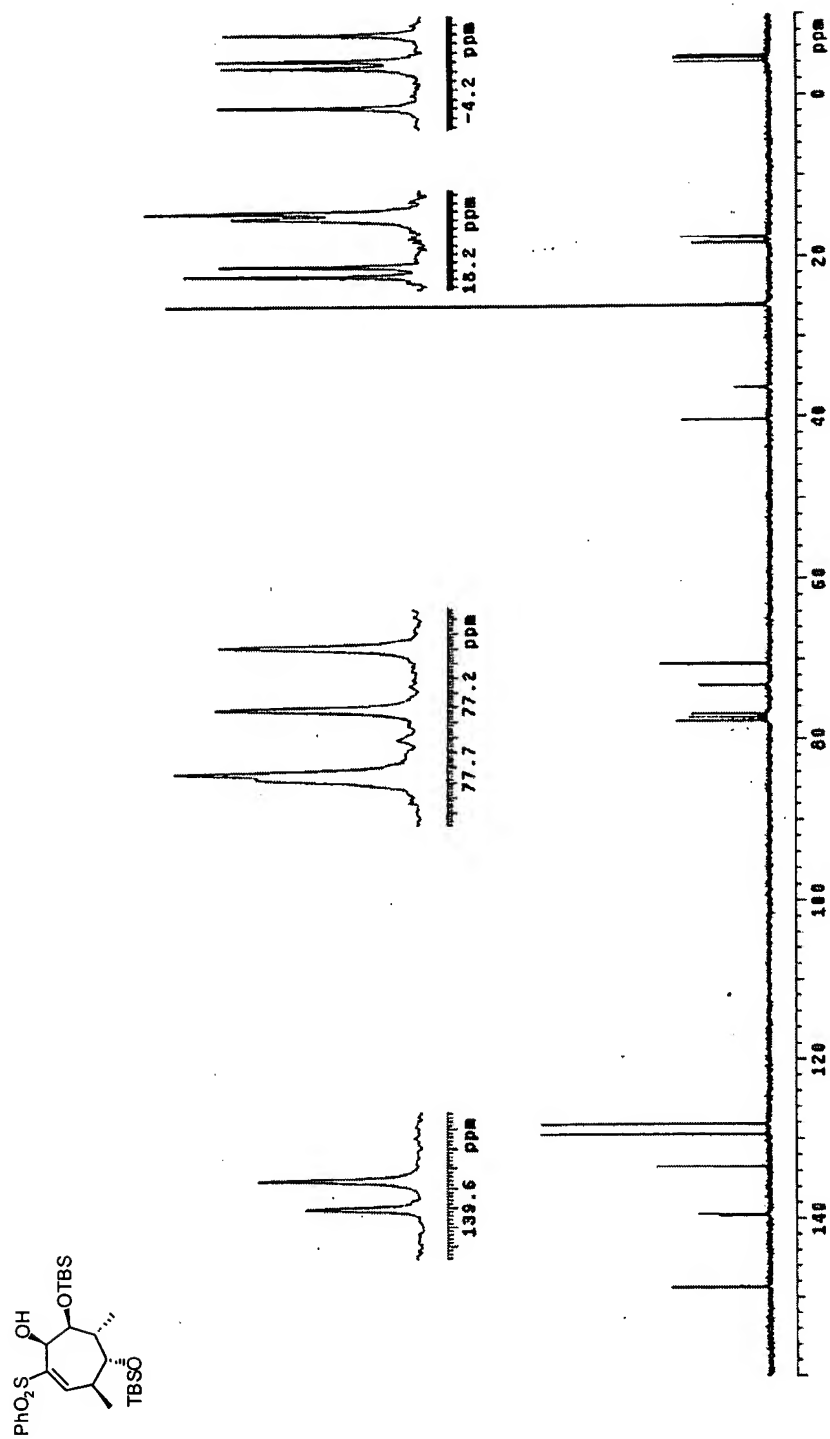
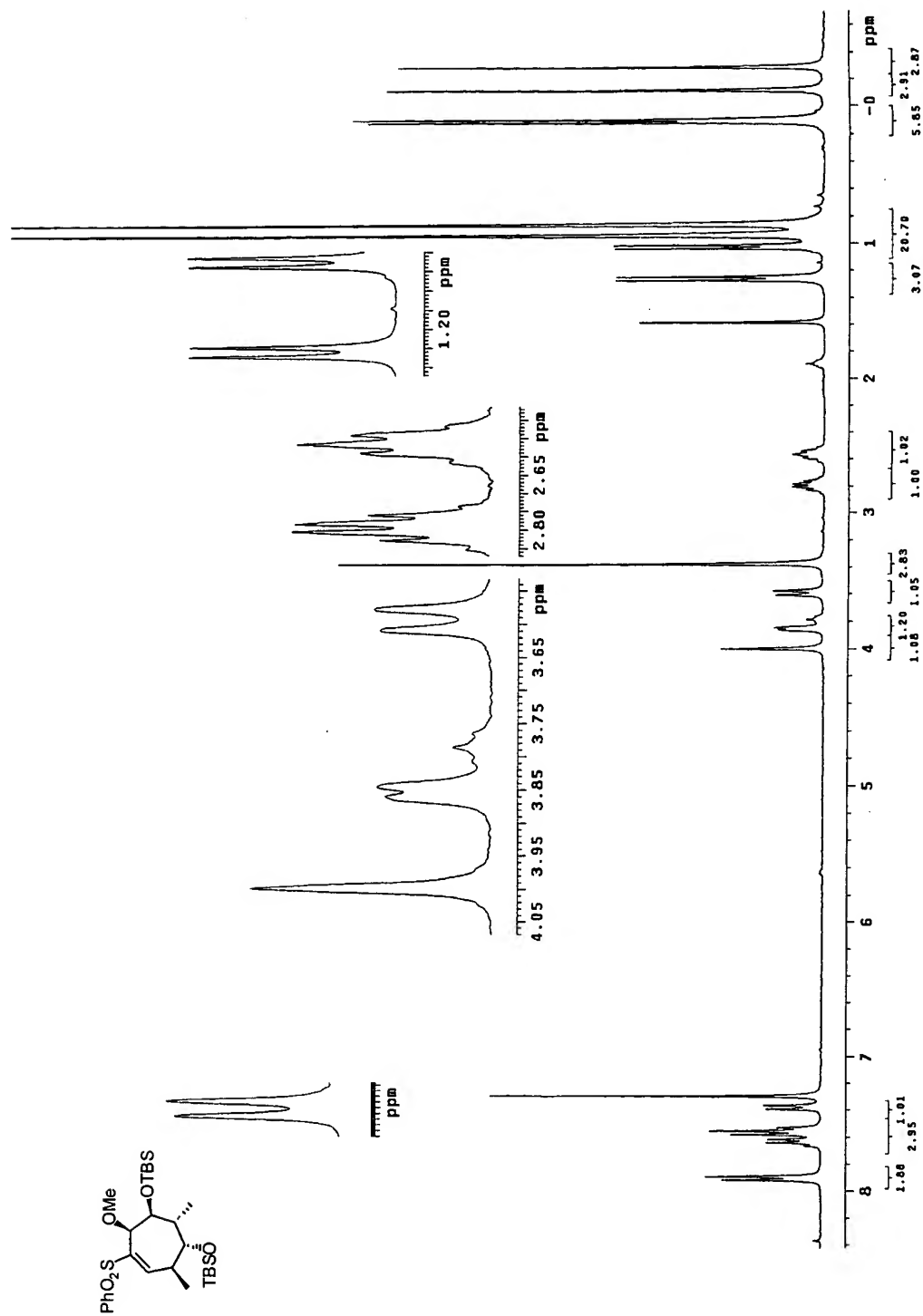
300MHz <sup>1</sup>H NMR of compound 52 in CDCl<sub>3</sub>

FIGURE 8 (Cont'd)



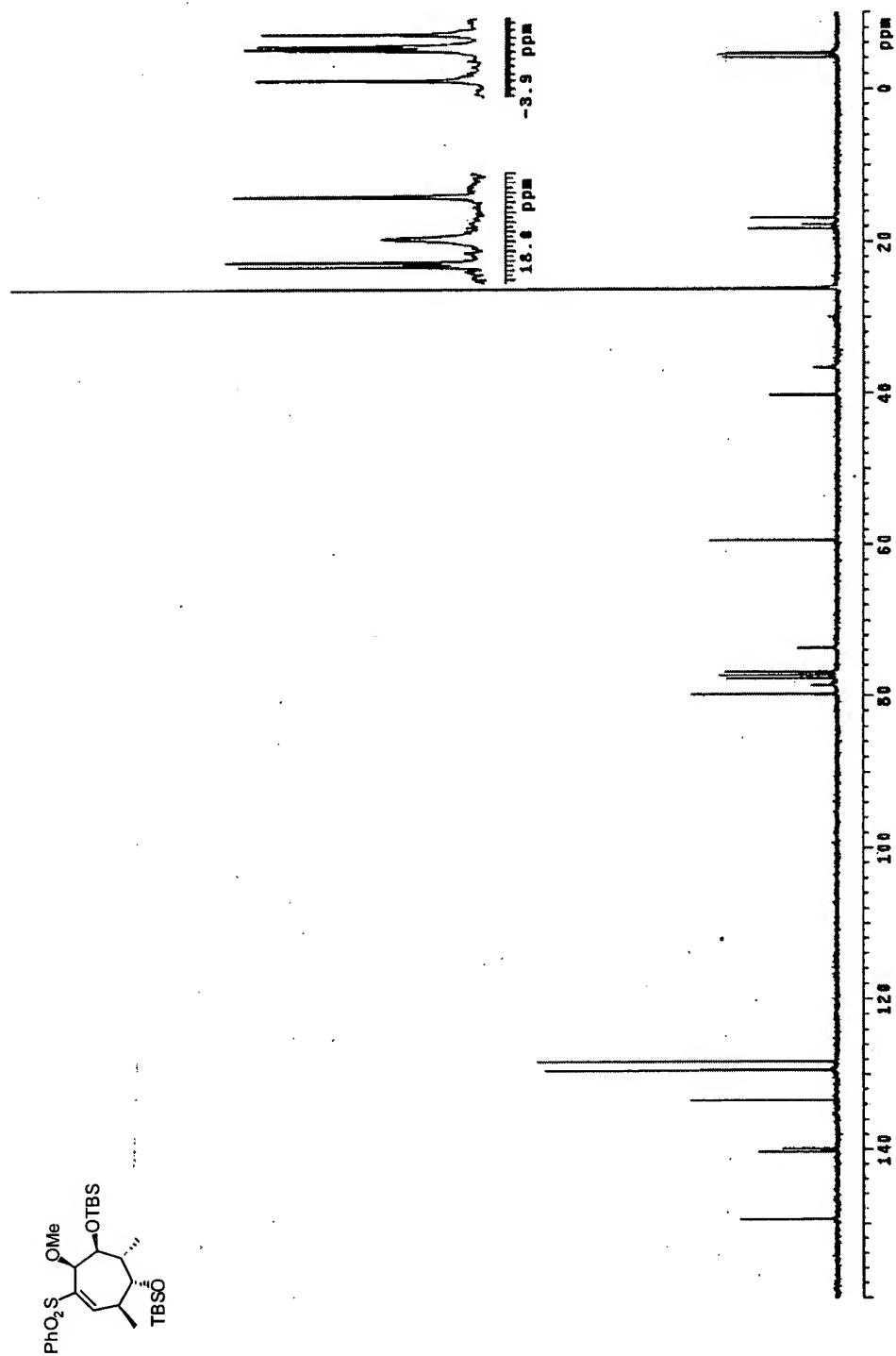
75MHz  $^{13}\text{C}$  NMR of compound 52 in  $\text{CDCl}_3$

FIGURE 8 (Cont'd)



300MHz  $^1\text{H}$  NMR of compound 53 in  $\text{CDCl}_3$

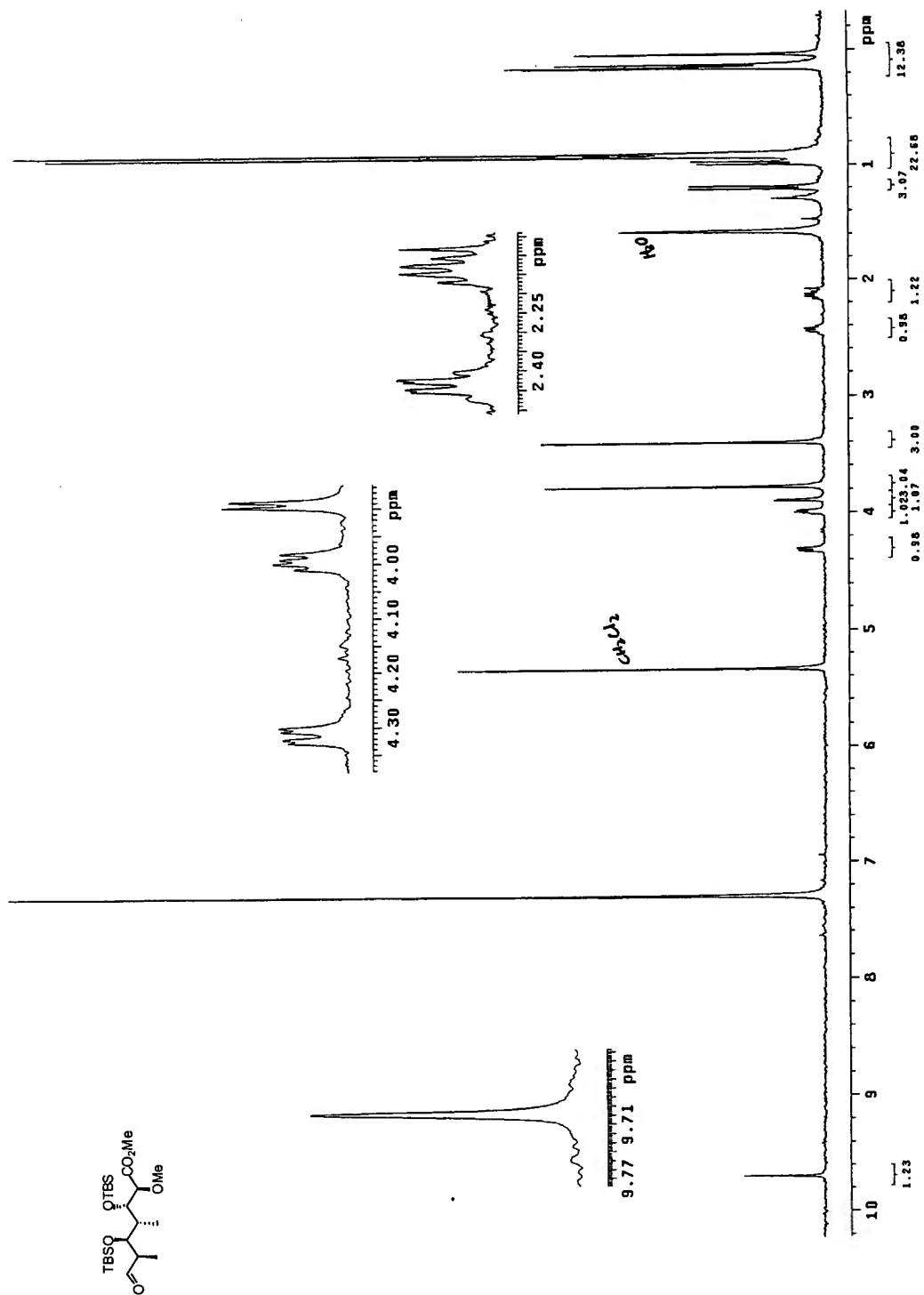
FIGURE 8 (Cont'd)



75MHz  $^{13}\text{C}$  NMR of compound 53 in  $\text{CDCl}_3$

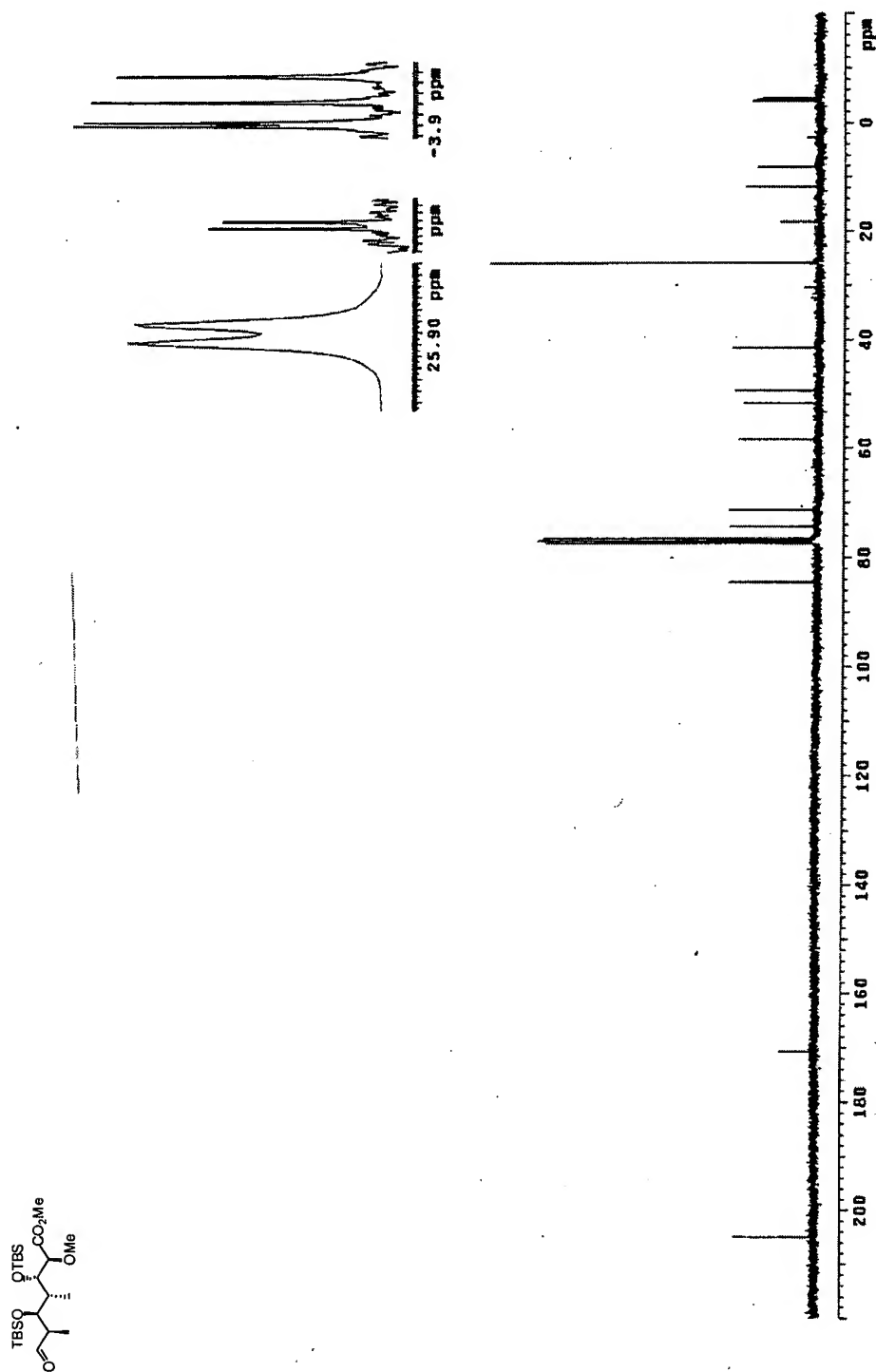


FIGURE 8 (Cont'd)



300MHz  $^1\text{H}$  NMR of compound 51 in  $\text{CDCl}_3$

**FIGURE 8 (Cont'd)**

75MHz  $^{13}\text{C}$  NMR of compound 51 in  $\text{CDCl}_3$